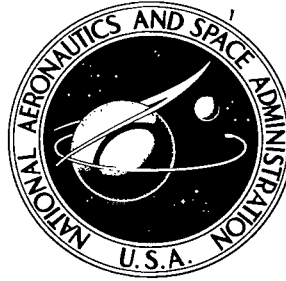


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NUMERICAL METHODS IN THE THEORY OF RAREFIED GASES

Edited by V. P. Shidlovskiy

*Computer Center, USSR Academy of Sciences
Moscow, 1969*



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NUMERICAL METHODS IN THE THEORY OF RAREFIED GASES

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v Teorii Razrezhennykh Gazov."
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AUTHOR'S FOREWORD

Since the second half of the last century, when Maxwell and Boltzmann made clear the principles of the theory of gases, the main problem on which the kinetic theory has centered has been the solution of the Boltzmann equation. The efforts of many authors resulted in a high level of understanding of the principal aspects of the kinetic theory, and the solution of a number of problems which both interested scientists and were of practical interest. The rapid growth of computer technology opened new possibilities for solving these problems. Nevertheless, at present there exists no general or sufficiently efficient method for solving the Boltzmann equation. /3

In 1965, when a new BESM-6 computer began operation, a small group of staff members of the Computer Center of the Academy of Sciences of the USSR began investigations in the area of the kinetic theory, attempting to develop methods for solving the mechanics problems involved in rarefied gases. This collection reflects the first results obtained by the authors during 1965-1967.

Several lines of investigation were pursued. The aim of the first was to find accurate solutions for the Boltzmann equation. These solutions can be used for testing the general solution methods which are difficult to obtain theoretically. This includes the work of V. A. Rykov and F. G. Cheremisin, as well as the work on spatially uniform flows in the kinetic theory done by A. A. Nikol'skiy, and the work of V. A. Rykov and T. I. Chukanov on the relaxation of a mixture of gases, which, aside from the kinetic theory, is of great interest from the standpoint of chemical kinetics.

The second direction is associated with the search for direct numerical solutions to the Boltzmann equation problem (F. G. Cheremisin, Ye. F. Limar). Some difficulties which arose in developing a general method for the solution of Boltzmann equations may be overcome by purely analytical methods (Ye. M. Shakhov).

Investigations of the flow of rarefied gas include the problem of interaction of gas particles with the surface of solids. The results obtained in this area are illuminated in the article by A. A. Pyarnpuu. /4

The collection also contains work which deals with the use of the classical Enskog-Chapman method as applied to the flow of chemically active gas mixtures (B. V. Alekseyev, B. V. Alekseyev and V. R. Yanovskiy).

It is hoped that this work will be of use to specialists and to all those who are interested in the theory of rarefied gases, and that it will facilitate rapid solution of many theoretical and practical problems.

The authors wish to express their deep gratitude to A. A. Nikol'skiy, who directed the work on rarefied gases at the time when it was organized and who obtained the initial results, and to O. S. Ryzhov for the discussion of the work and useful suggestions. It is perhaps superfluous to say that the authors are indebted to a large extent to each other for mutual success.

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NUMERICAL METHODS FOR SOLVING THE BOLTZMANN EQUATION

(A Review)

Ye. F. Limar, Ye. M. Shakhov, and V. P. Shidlovskiy

Introduction

The integro-differential Boltzmann equation, which is the principal equation in the kinetic theory of gases, was obtained by Boltzmann approximately one hundred years ago. Since that time, significant success has been achieved in the investigation of this equation by means of analytical methods, the principal ideas of which were proposed long ago by Maxwell and Boltzmann. In the main, these achievements pertain to the investigation of flow close to the limiting condition of a continuous medium. Subsequently, completely new possibilities arose associated with the use of high-speed computers. Since the development of the new technology requires most accurate data retrieval just in that range of characteristic parameters where the accepted analytical methods are not applicable, the first numerical methods for the solution of the Boltzmann equation began to appear. In the recent monograph of M. N. Kogan [1], a review of such methods is given. However, after this monograph was published, a new interesting work appeared in literature in which the earlier described methods were either modified or new methods were proposed.

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In the case of numerical solution of the Boltzmann equation, great difficulties arose and until this time attempts were made to solve only the simplest problems. One of the first exact solutions of the Boltzmann equation was given by V. A. Rykov [2], and V. A. Rykov and T. N. Chukanova [3] for the relaxation problem of the distribution function which depends only on the velocity modulus in homogeneous space. In reference [2], it was shown that the multiplicity of the collision integral can be reduced to two; this enables one to solve the problem by ordinary methods with great accuracy. Numerical methods exist for solving more complex one-dimensional and even two-dimensional problems, however, in the majority of cases, it is almost never possible to indicate the degree of accuracy of the obtained solutions, or the accuracy in approximating the original Boltzmann equation.

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* Numbers in the margin indicate pagination in the foreign text.

At present, the Monte Carlo statistical sampling methods are developed more than any other and these have given the most interesting results. These methods were first proposed by Alder, Wainwright, and others [4, 5], who made the first attempt to solve the relaxation problem in gases in a homogeneous space. The Monte Carlo methods were further developed by Haviland and Lavin [6, 7, 8], Bird [9-12] as applied to the boundary problem in the theory of rarefied gases.

The review considers the methods which show promise in solving the Boltzmann equation in a broad range of Knudsen numbers. Therefore, we shall not touch upon such methods as the Monte Carlo method in the theory of one collision for flow close to free molecular flow. It has been described in great detail in M. N. Kogan's monograph [1], and in the work of V. A. Perepukhov (for example, see reference [13]), and it already became a working method for calculation of the hydrodynamic flow past a body of complex shape under conditions close to free molecular flow.

The discrete velocities method, which performed very well in solving the problem in the theory of radiation, is used now successfully for solving the kinetic model equation. The review briefly presents the work of B. Hamel and M. Wachman, which in fact is the first attempt to apply this method to the solution of the Boltzmann equation.

Finally, the last part of this review presents certain new approaches to the solution of the Boltzmann equation; these were developed by F. G. Cheremisin [14] and Ye. M. Shakhov [15, 16], and are published in this collection.

1. Monte Carlo Method

These are generally the methods in which molecular motion is modeled on a high-speed electronic computer. However, one can also include here those methods in which the Monte Carlo method itself is used only in calculation of the Boltzmann collision integral.

Since the gas consists of a large number of molecules, its motion can be modeled by two methods: either using the properties of the symmetry of flow, limiting oneself only to modeling of the phenomenon in an extremely thin layer (here the necessary number of molecules to be considered becomes acceptable) or one models the real molecules as spheres of significantly larger diameter, such

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as will produce the necessary Knudsen number in calculations with a relatively small number of spheres.

Haviland-Lavin Method. One of the Monte Carlo methods was first described in the work of Haviland and Lavin [6, 7]. Using this method, problems of heat transfer between parallel plates [6] and later the problem of the structure of shock waves [7] were solved. The most detailed description of the method and the results was given in the book [8]. In the above-mentioned problems the distribution function depends on two velocities u_x , V and one physical space coordinate x . The solution of the problem by this Monte Carlo method is somewhat analogous to the following iteration for solving one dimensional stationary equations

$$u_x \frac{\partial f^{(r)}(x, u)}{\partial x} = \int_{-\infty}^{+\infty} d\vec{V} \int_0^{b_{\max}} b db \int_0^{2\pi} d\epsilon g \{ f^{(r)}(x, \vec{u}', V) \times \\ \times f^{(r-1)}(x, \vec{V}') - f^{(r)}(x, \vec{u}) f^{(r-1)}(x, \vec{V}) \},$$

where, as usual $\vec{g} = \vec{u} - \vec{V}$; b , ϵ - collision parameters; primed variables refer to the velocities at the collision. In reality the iteration process is modeled as follows.

The physical space along the x coordinate is subdivided into cells, which have the shape of a parallelepiped with the area of the base ΔA and the altitude Δx . The velocity space u_x , V is subdivided into cells which can be represented in the form of disks of radius V and thickness ΔV and height Δu_x . The phase space cell has a volume $2\pi V \Delta V \Delta u_x \Delta A \Delta x$. All of the molecules which have one of velocities $|u_x| > u_{x0}$ or $V > V_0$, fall in the end cells; here u_{x0} and V_0 are the boundaries of next to the last cell. Inside the cell the distribution function value is considered to be constant and equal to the distribution function value in the center of the cell.

The molecules with the distribution function of the $(r - 1)^{\text{th}}$ approximation are known as field molecules; the molecules by means of which the distribution function of the r^{th} approximation is sought are known as the test molecules. The motion and collision of test molecules is modeled in a medium of field molecules. The test molecules are chosen at the boundary by a random

method in accordance with the known distribution density of particles which fall outside the boundaries. Here it is necessary to renormalize the distribution function in order to obtain the probability density, the integral of which is equal to unity with respect to all velocities. The methods for obtaining the random numbers with the known distribution density have been described in detail in the book [17].

Subsequently, for the chosen particle the flight time without collision in a given space cell is selected by a random method. If the collision occurs inside the cell then, by the random method in accordance with the field particle density distribution, the velocity for the field particle which must collide with the test particle is selected, and the collision calculation is performed. The test particle which we are observing will acquire a new velocity and for it a free path time is again sampled. If the particle crosses the boundaries of the cell without any collision, then in the next cell the free path time is again sampled. The number of test molecules, the motion of which is observed from the moment of crossing the boundary to the moment of crossing the boundary again, must be such that the obtained distribution function has a sufficiently small fluctuation.

It is assumed that the distribution function in this cell is proportional to the time which is spent by the test particles in this cell. In the course of the whole iteration process, the time spent by the test particles in each cell of the phase space is accumulated. If this quantity is normalized in each cell by an appropriate method, then we shall obtain a density distribution in the r^{th} approximation. After all of the sampling in sequential iteration is completed the cross-sectional area ΔA of the physical space cell is selected in order to renormalize the obtained distribution function.

In solving the heat transfer problem ΔA is selected in such a way that the average density of the test particles in the selected space between two walls is of predesigned magnitude. In the study of the structure of a shock wave ΔA is selected on the basis of the condition that the mass flow of test molecules through a unit area at the boundary corresponds to the actual mass flow.

At the end of each iteration moments of the distribution function are calculated. In the calculation process, it is necessary to remember the distribution function of two iterations. The iteration process is completed

when the determined moments of the distribution function in two successive iterations coincide.

Haviland and Lavin solved the heat transfer problem between two parallel plates and the problem of the structure of shock waves for solid spheres and Maxwell's molecules.

The calculation errors may be subdivided into two classes, statistical and systematic. The systematic errors are associated with the choice of the dimensions of the cell, replacement of the distribution function by a step function, inaccurate calculation of the integral, which represents the collision frequency, and other deterministic effects. The statistical errors, which occur due to the limited number of games played, decrease as $1/N^{-1/2}$, where N is the number of games. Their effect may be determined experimentally.

In the majority of cases in solving these problems nonstatistical fluctuations are observed, the magnitude of which is significantly greater than the magnitude of the assumed statistical fluctuations. The structure of these fluctuations depends, primarily, on the form of the zero iteration. Apparently their occurrence is associated with the Markoff's nature of the iteration calculation process.

Such methods have one more drawback. When the Knudsen number is decreased significantly, the computation time increases and the accuracy of the method decreases. Apparently, the Monte Carlo methods of this type give the best results in the investigation of free molecular and nearly free molecular flows.

In solving even one-dimensional problems by the Monte Carlo method, it is necessary to have access to a large operational memory. For pseudo-Maxwell's molecules, the collision cross section of which has the form $\sigma = \sigma_0 g/g$. V. I. Vlasov [18] has shown that one can significantly reduce the size of the required memory. For these molecules the collision frequency is independent of particle velocity, and the probable velocity of the molecules which collide with the test molecule is proportional to the distribution function of the molecules in a given cell of the physical state. In reference [18], the velocity of the test molecules which passed through a given cell or physical state was remembered with $1/V$ probability, and when the next collision was sampled, this velocity was taken as the velocity of the molecule which collides

with the test molecule. In fact, in solving the heat transfer problems between plates, seven molecules were remembered in each of the geometric cells. The obtained results were practically coincident with the results of Lavin and Haviland.

In the work of Perlmutter [19] another method is proposed for reducing the required memory of the electronic digital computer. In solving the flow problem with the Couette method, analogous to the Haviland and Lavin method, it was proposed that the distribution of field molecules has the form of a double-flow Maxwell distribution, first proposed by Lees [20]. In this case, it is necessary to remember only four parameters ρ_+ , c_+ , ρ_- , c_- , which enter in this distribution for each of the cells of the physical state. The meanings of these parameters are: density and temperature of molecules with positive or negative projections of the velocity upon the coordinate axis, perpendicular to the walls respectively. Perlmutter's results coincide with the results of Lavin and Haviland.

The calculation method proposed by Perlmutter is not universal since it is strongly dependent on the choice of the approximation function. However, the idea of more accurate approximation of the distribution function inside the phase space cell apparently deserves some attention.

The Bird Method. A somewhat different Monte Carlo method was proposed by Bird [9-12]. In contrast to the method used by Haviland this method does not contain iterations. The stationary condition is obtained as the limit of the nonstationary flow, which occurs upon instantaneous introduction of a body into a homogeneous flow. After a certain period of time, a steady state is achieved. The value of the stationary flow may be calculated in the course of long time intervals by averaging the quantity in time in order to reduce random scatter. In reference [9], the time for the establishment of equilibrium of the translational degrees of freedom was evaluated. In reference [10, 12], the structure of the shock wave in a gas consisting of solid spheres was calculated. In reference [11], the results are given for the calculations of aerodynamic flow past a cylinder, a sphere and a plate. However, in the subsequent

work [12], the author shows that certain procedures used in [10, 11] were incorrect¹.

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The essence of the method is as follows. The physical coordinate space is subdivided into cells. Several thousand molecules are taken and by the random method, in correspondence with preassigned distribution functions, a configuration of molecules is selected for the initial moment of time. It is assumed that inside the physical space cell all of the molecules have the same coordinates. The velocity components of all of the molecules are also remembered. The process of motion and collision of molecules is subdivided in time; it is considered that during the time interval Δt_m only collisions in all of the cells of the physical state take place, and since the relative position of the molecules within the cell of physical space is neglected, the probability of their collision depends only on their relative velocities. A pair of molecules in the considered physical space cell is selected by a random method. It remains there with a probability proportional to relative velocity. If the pair remains there, the collision calculation is carried out and the new velocity components of the colliding molecules are recorded. The number of collisions is determined as the quotient from dividing Δt_m by Δt , where Δt is the mean time between collisions for a given cell of the physical space per molecule. The time interval Δt_m is taken to be significantly small than the average time between collisions.

After all the collisions have been completed, the overall time is increased by Δt_m and all molecules are moved by an appropriate distance. At the boundaries the molecules are either generated with a corresponding density distribution or are annihilated if they fall outside the boundaries of the given region.

In calculating shock wave structure, it was discovered that the results are little dependent on the choice of cell dimensions. The comparison of the density profile when $M = 1.5$ with the density profile obtained by the Navier-Stokes equation shows that nonstatistical oscillations behind the shock wave are small. Calculations were made for the shock wave

1. Apparently, as a result of this, some individual results in [11] are not even in qualitative agreement with the already available data. However, satisfactory results in [12] lead us to believe that after correcting the error this method can produce more accurate results.

with Mach numbers ranging from 1.5 to 10. The longitudinal and transverse distribution functions are represented at several points of the shock wave front. When the Mach number is ten, the distribution function has two maxima, and the density profile of the shock wave is not as steep as predicted by the Navier-Stokes equation or the Mott-Smith solution. The time required for calculating shock wave structure on a KDF-9 computer was 20 minutes.

The Nordsieck Method. In solving Boltzmann equation by the iteration method, the collision integral calculation is the most difficult. Nordsieck [21] proposed a Monte Carlo method for the calculation of the complete five-dimensional collision integral for solid spheres in axially symmetric flows. Here, the collision integral in velocity space depends on two parameters u_x , V (where u_x is the velocity of molecules along the axis of symmetry and V is the velocity of molecules perpendicular to the axis of symmetry). In order to accelerate the count, eight uniformly distributed quantities are immediately generated (three quantities give the value of the parameter for which the integral is calculated, while three others give a point in which the integral function is being calculated, the two remaining quantities are the collision parameters of the molecules), and the integrals for all 256 values of u_x and V are calculated (in the case of fixed value of all physical coordinates). This allows one to increase the number of tosses through the use of symmetry of collisions without additional arithmetic operations. The results of the calculations of the integrals are subsequently smoothed by the least squares method.

The reference shows preliminary results of the calculations of the problem of relaxation and shock wave structure. In reference [22], it was shown by means of this program how the Mott-Smith method solution for shock wave structure gives a nonsensical solution. Unfortunately, in the work which is available to us, there is very little data to judge the advantages of this method as compared with other Monte Carlo methods.

One more variation of the Monte Carlo method was proposed by Gentry, Harlow and Martin [23] for modeling a flow with a transverse velocity gradient, when the particles are moving between two plane-parallel walls. However, due to the limitations of the computers, the numerical experiments which were described were performed for an assembly of two-dimensional molecules, which

indicates the low economic efficiency of the method.

The Monte Carlo method for solving the relaxation problems in homogeneous space. /13 One of the simplest problems for the Boltzmann equation is the relaxation of some distribution function in homogeneous space to the Maxwell distribution function. In the work of Alder and Wainwright [4, 5], the solution of such a problem was modeled as follows: the motion and the collision of a small number of molecules (of the order of one hundred) in a cubic cell was considered. If any of the molecules crosses the boundary, it is considered that an exactly identical molecule enters the cell through an opposite face of the cubic cell (periodicity condition). In this modeling process coordinates and velocities of all molecules are remembered. The ratio of the number of molecules in a given velocity interval to the number of molecules in this velocity interval at equilibrium is a function of the number of collisions. The same problem was solved by Bird by an analogous method [9], but in contrast to the work of Alder and Wainwright, he kept only the velocity of molecules in the memory. This enabled him to obtain results with high accuracy. In general, they are in good agreement with the results of [5]. An interesting conclusion was drawn: the high-velocity molecules undergo relaxation most slowly, while molecules with velocities close to the root-mean-square velocity undergo the most rapid relaxation.

The method developed by Alder and Wainwright with some modification was used for the investigation of relaxation in a mixture of gases by Polak and others [24, 25]. A comparison with the exact solution of the Boltzmann equation [3] for these initial data has shown satisfactory accuracy of the method.

Ioshizawa [26] solved the problem of the relaxation of chemically reacting gases by the Monte Carlo method. Instead of considering the collision of three bodies, the activated molecule method was used. Only three types of collisions were considered: elastic, inelastic and activated; all molecules and atoms were modeled by solid spheres. The relaxation phenomenon was modeled by observing the collisions of a small number of particles (of the order of 50). For each type of particle, three components were remembered: velocity, type of particle and its internal energy. Initially, the type of particle was drawn, followed by its velocity and mean free path and finally the internal energy of the molecule when necessary. Subsequently, by an analogous method, the

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characteristic of the second particle was drawn and the velocity of both particles after collision was calculated; the results of the reaction were put into the memory. The behavior of this particle was observed over a period of time Δt , which is significantly shorter than the relaxation time. After the histories of all test particles were observed, new distribution densities of particles and internal energy were calculated. From time to time, the values of certain moments were calculated and printed out. Due to the small number of particles large fluctuations were observed, particularly near equilibrium. The author expresses the opinion that these fluctuations are associated with the Markoff nature of the proposed Monte Carlo method.

2. Discrete Velocities Method

The discrete velocities method was proposed by Chandrasekhar and was utilized successfully in solving problems in the theory of radiation and the theory of neutron transport. In problems on the flow of rarefied gases, it was first used in the work of Broudwell [27, 28], but only at a very approximate level. At present, the discrete ordinate technique is used successfully in solving the model Krook equation [29].

B. Hamel and M. Wachman using this method for the linearized Boltzmann equation solved the problem of Couette flow [30], and then a nonlinear relaxation problem [31].

Let us consider the last work in greater detail, since this in essence is the first attempt to use the discrete velocity technique for the nonlinear Boltzmann equation.

Let $f(\vec{V})$ be the distribution function for which the Boltzmann equation can be written as usual. The integral is calculated by the reiteration method, where in calculation of the integral from the collision parameters quadrature, Laguerre equations were used, and in calculation of the velocity integrals Gauss-Hermite quadrature equations were used. After all of the integrals were calculated in all nodes, the derived system of differential equations was solved by the Lantsosh method. Thus, the value of the distribution function at the moment $t + \Delta t$ was calculated.

Let us introduce the function $\Psi(\vec{V})$ by the following method:

$$f(\vec{V}) = e^{-V^2} \psi(\vec{V}).$$

Then the Boltzmann equation will acquire the form

$$\frac{d\psi(\vec{V})}{dt} = \int_{-\infty}^{+\infty} \int_0^{2\pi} \int_0^{\pi/2} e^{-\xi^2} [\psi(\vec{V}') \psi(\vec{\xi}') - \psi(\vec{V}) \psi(\vec{\xi})] |\vec{\xi} - \vec{V}| \sin\theta \cos\theta d\theta d\epsilon d\vec{\xi}. \quad /15$$

As the initial condition when $t = 0$ we stipulate $\Psi_0(V)$.

In this work, the discrete ordinate technique was adapted to the solution of this very type of problem with the initial data. In the $(n - 1)^{\text{th}}$ interval, the calculated distribution function $\psi(\vec{V})$ is remembered in some network of \vec{V} values. Subsequently, the collision integral is calculated on the basis of this function. In such calculation, it is necessary to know the value of the distribution function outside the nodes; therefore, it is necessary to use the interpolation method or extrapolation formulas. The results of calculations show that the selected network gives good results for ψ functions close to constant (i.e., for the initial function close to the Maxwell function). Otherwise, even when t is equal to one collision time, the density and temperature decrease by 10% and reveal a tendency to further decrease. Therefore, calculations are carried out until $t = 1$, although on the basis of the extrapolative evaluation of the author complete relaxation occurs at approximately $t = 4$. It is noted in the work that normal stress behaves in the same manner as indicated by the model equation.

3. Other Methods for Solving the Boltzmann Equation

F. G. Cheremisin and Ye. M. Shakhov, staff members of the Computer Center of the Academy of Sciences of the USSR, proposed other methods for solving the Boltzmann equation, significantly different from those which were discussed above.

F. G. Cheremisin [14] proposes the use of the iteration process for the kinetic equation, written in the integral form, which includes the probabilities of free paths of the molecule.

Assuming that the n^{th} iteration is sufficiently close to the accurate solution, the moment of the distribution function in an approximate form of the function itself is expressed taking into account the boundary conditions in the

form of a network of successive approximations directly through the distribution function of the zero approximation. Since the zero approximations for the distribution function as a function of the velocity of molecules may be assigned in analytical form, such an approach gives the possibility of solving the problem on an electronic digital computer with limited operational memory. /16

However, the essence of the proposals of F. G. Cheremisin is not limited to the reduction of the required machine memory. In order for the machine time, which increases inadmissibly with an increase in the number n , to be applicable in practice, the Monte Carlo method with a sufficiently small number of trials (where the number could be smaller as the number of iterations of the distribution function becomes smaller, from which the integrals are calculated) is proposed [14] for calculations of the internal integrals from molecular velocity and collision parameters. The calculations which were made by the author for the relaxation and the shock wave structure problems have shown that when the number of random points for the calculation of the integrals of the lowest link in the chain (from the initial distribution function), is several tenths, and sometimes several units, a satisfactory accuracy of the result is achieved. The integration of space variables and calculation of the distribution functions moments are carried out by the regular method.

Apparently, the number of iterations n is smaller, the closer the initial function is to the precise value. As the initial approximation, it is proposed that solution of Krook's relaxation equation be used. The author hopes that his proposed method for numerical solution of the Boltzmann equation will allow solution of the problem of the theory of rarefied gases using modern computers in a practically reasonable time.

Ye. M. Shakhov proposed a fundamentally different method for solving the Boltzmann equation [15, 16]. The difficulties associated with the solution of the Boltzmann equation result not only from the large number of independent variables, but also from the complex structure of the collision integral. It was proposed in [15] that the collision integral be approximated in the moment sense (i.e., so that the several first moments from the approximate and from the Boltzmann collision operators would coincide). The equation for the distribution function with an approximate, in the moment sense, collision operator is an equation approximating the Boltzmann equation. Consequently, the

distribution function which satisfies this equation is an approximate solution of the Boltzmann equation. It is assumed that the approximation accuracy increases with an increased number of moment relationships for the collision operator.

Apparently, in such an approximation several first moment equations from the approximate kinetic equation and from the precise Boltzmann equation will coincide, and there will be as many coincident equations as there are first moment relationships fulfilled for the collision integral. Since in the rarefied gas mechanics, the principal interest lies in a few first moments of the distribution function in that region which makes the principal contribution to the magnitude of these moments, one can hope that in the approximation one should limit oneself to moment relationships which include power monomials of the molecular velocity components not higher than of the third degree. The results of the author's calculations for the relaxation problem confirm this viewpoint. /17

The form of the approximate collision operator is not determined by moment relationships of the type described above.

The approximation is directly reduced to replacing the reverse collisions integral and collision frequency by suitable expressions dependent on the molecular velocities and on some set of macroscopic quantities. The macro-parameters which are included in the reverse collisions integral are determined by the moment relationships. The collision frequency is approximated with sufficient accuracy for many problems by the corresponding expressions for the local-Maxwell distribution function. In case of necessity, deviations from this expression may be found by utilizing the moment relationships separately for the direct collisions integral. Another method for approximating collision frequency through the distribution function moments involves expansions for low and high velocities.

The integrals from the collision integral may be expressed with sufficient accuracy through the distribution function moments; this significantly reduces the required computation time.

Thus, the approximating equation in each approximation has a structure similar to the structure of the Krook relaxation equation in that the reverse collision integral and collision frequency are explicit functions of molecular

velocities and distribution function moments. Use of the discrete velocities method is proposed for numerical solution of the approximate equation in any approximation.

Summary

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The review considers the principal attempts to obtain the numerical solution or modeling of the Boltzmann equation over a broad range of Knudsen numbers. The review of these results shows that only initial steps have been taken in the area of the development of numerical methods. The proposed methods are at different stages of their development and many require a significant improvement.

In the presently most popular Monte Carlo methods, the equivalency of the obtained solutions and the solution of the Boltzmann equation has not yet been proven. One can say that the proposed method is quite logical and the results appear reasonable. However, in all the solutions associated with these methods, nonstatistical fluctuations occur in the area of high densities; the nature of these fluctuations is not yet clear. The Monte Carlo methods are not well suited in the area of small Knudsen numbers. In this case, the distribution function must be close to the local-Maxwell function, and the collision integral must be close to zero. Here all of the calculations associated with collisions are conducted too coarsely, which leads to insufficiently accurate distribution function calculation. It is possible that this in fact determines the fluctuations.

Among the Monte Carlo methods, the Bird method appears to be most attractive, since it is more directly related to the Boltzmann equation. However, it also has the same drawbacks. Like other Monte Carlo methods, it gives the best results under the conditions which are close to the free molecular state.

The Nordsieck method is unique among other Monte Carlo methods, but it is still difficult to judge its merit due to the unavailability of the results obtained with it.

All of the Monte Carlo methods are characterized by slow convergence and one cannot expect to obtain highly accurate results with their use. Great possibilities are afforded in this sense by the deterministic methods. These

methods include the discrete ordinate technique. The direct use of this method for solving the Boltzmann equation shows that in order to obtain the required accuracy exceedingly large computer times are required in calculating the collision integral. The use of approximating equations in combination with the discrete velocities method will possibly improve computation accuracy and reduce the required memory volume.

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In summary one should say that all the methods considered in this review are applicable at best to solution of one-dimensional problems. The possibility for the practical applications to the solution of two-dimensional problems in the theory of rarefied gases has not yet been proven.

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A study of the simplest precise solutions of the Boltzmann kinetic equation was undertaken in [1-3].

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For this solution it is characteristic that in going to the characteristic velocities of particles, the dependence of the distribution functions on spatial coordinates vanishes.

Isolation of such a class of spatially homogeneous solutions is of interest due to the significant reduction in the number of independent variables, which permits the use of electronic digital computers for obtaining numerical solutions of the kinetic equation.

In this work a functional equation is derived for a spatially homogeneous distribution function and examples of spatially homogeneous gas motions are considered. Numerical calculation was conducted for one such motion with the use of a model equation.

1. Determination of Spatially Homogeneous Solution

In this section we shall depart temporarily from the Boltzmann equation and introduce the concept of a spatially homogeneous solution of some equation,

$$L(f) = 0 \quad (1)$$

where $L(f)$ is some operator of the sought function $F(t, x, y, z)$, where t is the time and x , y , and z are space coordinates. This operator contains the derivative of f with respect to variable t only of the first order; no other assumptions are made about its form.

Equation (1) may be differential or integro-differential.

Assume that equation (1) allows formulation of the Cauchy problem with respect to variable t , and assume that a unique solution exists. We can consider the initial function assigned at the time $t = t_0$: /23

$$f(t = t_0, x, y, z) = f_0(x, y, z) \quad (2)$$

$$(-\infty < x < +\infty, -\infty < y < +\infty, -\infty < z < +\infty).$$

Definition 1. The Cauchy problem is called spatially homogeneous if, for any point (x_0, y_0, z_0) in the Oxyz system, there exist transformations of time, coordinates, and the sought function

$$\begin{aligned} t' &= T(t, x_0, y_0, z_0), \quad x' = X(t, x, y, z, x_0, y_0, z_0), \quad z' = Z(t, x, y, z, x_0, y_0, z_0), \\ y' &= Y(t, x, y, z, x_0, y_0, z_0), \quad f' = \Phi(t, x, y, z, f, x_0, y_0, z_0), \end{aligned}$$

dependent on this point (x_0, y_0, z_0) and when $t = t_0$ moving the point (x_0, y_0, z_0) to the origin of the new coordinate system $O'x'y'z'$ and the time $t = t_0$ to $t' = t_0$ so that equation (1) and the initial function (2), written in the new sought functions and variables, will coincide with the initial ones.

The new independent variables and the sought functions will be differentiated from the originals by primes. It is apparent from the definition that in the new coordinate system, whose origin at the time $t = t_0$ is placed at a randomly selected point (x_0, y_0, z_0) , we have a Cauchy problem identical to the case with the original coordinate system, i.e.,

$$L[f'(t', x', y', z')] = 0, \quad f'(t' = t_0, x', y', z') = f_0(x', y', z') \quad (-\infty < x' < +\infty, -\infty < y' < +\infty, -\infty < z' < +\infty).$$

The initial function of such a Cauchy problem will be called spatially homogeneous. Apparently, the transformation described in definition 1 must belong to the class of invariant transformations of equation (1).

Let the known invariant transformation of equation (1) be

$$\left. \begin{aligned} t' &= T(t, s_1, \dots, s_k); \quad x' = X(t, x, y, z, a_1, \dots, a_l); \\ y' &= Y(t, x, y, z, b_1, \dots, b_m); \quad z' = Z(t, x, y, z, c_1, \dots, c_n); \\ f' &= \Phi(t, x, y, z, f, d_1, \dots, d_q), \end{aligned} \right\} \quad (3)$$

where s_1, \dots, d_q are random constants.

Definition 1 requires that the following condition be fulfilled:

$$\left. \begin{aligned} T(t_0, s_1, \dots, s_k) &= t_0; \quad X(t_0, x_0, y_0, z_0, a_1, \dots, a_l) = 0; \\ Y(t_0, x_0, y_0, z_0, b_1, \dots, b_m) &= 0; \\ Z(t_0, x_0, y_0, z_0, c_1, \dots, c_n) &= 0. \end{aligned} \right\} \quad (4)$$

In general, these conditions enable us to consider only $k+l+m+n+q-4$ constants as random constants. Let us assume that they are random functions of parameters x_0, y_0, z_0 . /24

If the variables t, x, y, z are not explicitly in equation (1), it will remain invariant in the case of random change in the origin of both time t and coordinates x, y, z . Therefore, conditions (4) can always be

satisfied if one includes the transformation of the changes in the origin of variables t, x, y, z in equation (3).

Let us now use the transformation of (3) under the condition (4) in obtaining a spatially homogeneous initial function.

This will complete the formulation of a spatially homogeneous Cauchy problem for equation (1). The initial function $f_0(x, y, z)$ must remain invariant in the case of transformation (3), and obey condition (4). This requirement leads to a functional equation for determining $f_0(x, y, z)$:

$$\begin{aligned} f_0[X(t_0, x, y, z, a_1, \dots, a_l), Y(t_0, x, y, z, b_1, \dots, b_m), \\ Z(t_0, x, y, z, c_1, \dots, c_n)] = \Phi[t_0, x, y, z, f_0(x, y, z), d_1, \dots, d_q], \end{aligned} \quad (5)$$

where the random constants are functions of the parameters x_0, y_0 and z_0 . The solution of this equation defines the spatially homogeneous initial function. It follows that a spatially homogeneous Cauchy problem for equation (1) exists if there is an invariant transformation for equation (1) which satisfies condition (4) and if there is a solution of the functional equation (5).

The solution of the spatially homogeneous Cauchy problems for equation (1) will be called a spatially homogeneous solution.

Assume that we know the solution of the spatially homogeneous Cauchy problem

$$f = f(t, x, y, z). \quad (6)$$

Then the solution of the spatially homogeneous Cauchy problem after the transformation to the new variables t', x', y', z' , and of the sought function f' , will have the same form, i.e.,

$$f' = f(t', x', y', z'). \quad (7)$$

Applying the inverse transformation in the obtained solution (7) to the old independent variable and sought function, we must, due to the uniqueness of the Cauchy problem solution, obtain a solution for (6). It therefore follows that the function $f(t, x, y, z)$ must satisfy the following functional equation: /25

$$\begin{aligned} f[T(t, s_1, \dots, s_k), X(t, x, y, z, a_1, \dots, a_l), \\ Y(t, x, y, z, b_1, \dots, b_m), Z(t, x, y, z, c_1, \dots, c_n)] = \\ = \Phi[t, x, y, z, f(t, x, y, z), d_1, \dots, d_q], \end{aligned} \quad (8)$$

where $T(t, s_1, \dots, s_k)$, $X(t, x, y, z, a_1, \dots, a_l)$, $Y(t, x, y, z, b_1, \dots, b_m)$ and $Z(t, x, y, z, c_1, \dots, c_n)$ obey condition (4), and the random constants are the functions of the parameters x_0 , y_0 and z_0 . It should be noted that if a spatially homogeneous Cauchy problem exists for equation (1), due to the uniqueness of the Cauchy problem solution transformation (3), which satisfies condition (4), it must be mutually unique.

In solving equation (8), the random dependence of constants on parameters x_0 , y_0 and z_0 is made more specific, due to the known existence of a solution. It can be shown that if the solution of equation (8) exists, it has the form $f = \Psi[t, x, y, z, \tau(t, x, y, z)]$, where Ψ is randomly dependent only on the variables $\tau(t, x, y, z)$, where the following is valid for $\tau(t, x, y, z)$:

$$\tau(t, x, y, z) = \tau(t', x', y', z'); \quad \tau(t_0, x, y, z) = \tau_0 = \text{const},$$

where t' , x' , y' , and z' are defined by equation (3).

Substituting the solution of equation (8) into equation (1) and requiring the latter to be satisfied, we obtain an equation for determining the dependence of the sought function on variable τ with initial condition $\tau = \tau_0$.

Thus, the spatially homogeneous Cauchy problem is reduced to the Cauchy problem for some function dependent on only one variable.

This result, although presented for a homogeneous equation involving a given function of three coordinates and time, can easily be applied to the Boltzmann equation; this is done below in an examination of specific examples.

2. Consideration of Examples of Spatially Homogeneous Motions

The kinetic Boltzmann equation for the distribution function of molecular velocities of a monatomic gas has the form [4]:

$$\frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} + v \frac{\partial f}{\partial y} + w \frac{\partial f}{\partial z} = J(f), \quad (9) \quad \text{26}$$

where x, y, z are Cartesian coordinates; t is time, u, v, w are velocity components, and $J(f)$ is the collision integral.

The gas particles interact with each other according to $F = n/r^V$.

Let us first consider the case when the distribution function f depends only on one coordinate x , time t , and three velocity components u , v , and w . Equation (9) will be written:

$$\frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} = J(f). \quad (10)$$

Let us transform the sought function and variables

$$\left. \begin{aligned} t' &= t/a; \quad x' = x - x_0; \quad u' = a u; \quad v' = a v; \quad w' = a w; \\ f' &= a^\gamma f, \end{aligned} \right\} \quad (11)$$

where x_0 , a , and γ are random constants. After the transformation, equation (10) becomes

$$\frac{\partial f'}{\partial t'} + u' \frac{\partial f'}{\partial x'} = J(f') a^{1+\gamma+4(2-\nu)/(\nu-1)}.$$

During the transformation of the collision integral its property indicated in reference [1] was applied:

$$J[u, v, w, f(u, v, w)] = J[au, av, aw, f(au, av, aw)] a^{4(2-\nu)/(\nu-1)}.$$

Assuming that $1+\gamma+4(2-\nu)/(\nu-1) = 0$, we find that in transformation of (11) with $\gamma = (3\nu-7)/(\nu-1)$, equation (10) remains invariant. If we further consider a to be a function of the parameter x_0 , we can write the functional relationship for the spatially homogeneous solution $f(t, x, u, v, w)$:

$$f[t/a(x_0), x - x_0, a(x_0)u, a(x_0)v, a(x_0)w] = a^\gamma(x_0) f(t, x, u, v, w).$$

The solution of this equation has the form:

$$f = \exp(-\gamma\lambda x) \varphi[\exp(-\lambda x)t, \exp(\lambda x)u, \exp(\lambda x)v, \exp(\lambda x)w],$$

where λ is a random constant and φ is a random function of its arguments.

Let us note that $a(x_0) = \exp(\lambda x_0)$.

Substituting this solution into equation (10) we obtain

$$\frac{\partial \varphi}{\partial \tau} + \lambda u_1 \left(-\gamma \varphi - \tau \frac{\partial \varphi}{\partial \tau} + u_1 \frac{\partial \varphi}{\partial u_1} + v_1 \frac{\partial \varphi}{\partial v_1} + w_1 \frac{\partial \varphi}{\partial w_1} \right) = J(\varphi), \quad (12)$$

where

$$\begin{aligned} \tau &= \exp(-\lambda x)t; \quad u_1 = \exp(\lambda x)u; \\ v_1 &= \exp(\lambda x)v; \quad w_1 = \exp(\lambda x)w, \end{aligned}$$

i.e., we arrive at an equation for the function φ , now dependent only on four independent variables: u_1 , v_1 , w_1 play the role of new velocities and the parameter τ , which may be interpreted as time; the dependence on the

space coordinates disappears.

For equation (12), when $\tau = 0$, one should assign the initial function $\varphi = \varphi(u_1, v_1, w_1)$. This corresponds to the following initial function for f :

$$f(t=0, x, u, v, w) = \varphi_0[u \exp(\lambda x), v \exp(\lambda x), w \exp(\lambda x)] \exp(-\gamma \lambda x). \quad (13)$$

We calculate the initial density distributions n , velocities U , V , and W , and temperature T corresponding to (13):

$$\begin{aligned} n(t=0, x) &= \exp(-\gamma \lambda x) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \varphi_0(e^{\lambda x} u, e^{\lambda x} v, e^{\lambda x} w) du dv dw = \\ &= \exp(-\gamma \lambda x - 3\lambda x) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \varphi_0(u_1, v_1, w_1) du_1 dv_1 dw_1 = n_0 \exp[-\lambda x(\gamma + 3)]; \end{aligned}$$

$$U = U_0 \exp(-\lambda x); \quad W = W_0 \exp(-\lambda x);$$

$$V = V_0 \exp(-\lambda x); \quad T = T_0 \exp(-2\lambda x),$$

where n_0 , T_0 , U_0 , V_0 , W_0 are random constants, with n_0 and T_0 positive.

This motion differs from the motion considered in references [1-3] in that the density and temperature depend on the x coordinate.

Let us proceed to the formulation of a second example of spatially homogeneous gas motion.

Let the distribution function f depend on coordinate z , time t and three velocity components, u , v , and w . The Boltzmann equation becomes:

$$\frac{\partial f}{\partial t} + w \frac{\partial f}{\partial z} = J(f). \quad (14)$$

This equation allows an invariant transformation

$$\left. \begin{aligned} t' &= t; \quad z' = z - z_0; \quad u' = u \cos \varphi + v \sin \varphi; \\ v' &= -u \sin \varphi + v \cos \varphi; \quad w' = w; \quad f' = f, \end{aligned} \right\} \quad (15)$$

where z_0 and φ are random constants.

Transformation (15) shifts the origin of the physical coordinate system to point $(0, 0, z_0)$ and rotates the coordinate system in velocity space by the angle φ about the Ow axis. Assuming φ to be a function of the z_0 parameter, we can construct a functional equation for a spatially homogeneous solution corresponding to transformation (15),

$$\begin{aligned} f[t, z - z_0, u \cos \varphi(z_0) + v \sin \varphi(z_0), -u \sin \varphi(z_0) + \\ + v \cos \varphi(z_0), w] = f(t, z, u, v, w). \end{aligned}$$

Its solution has the form

$$f = f(t, u \cos kz + v \sin kz, -u \sin kz + v \cos kz, w), \quad (16)$$

where k is the random constant.

The dependence of φ on z_0 is as follows: $\varphi = kz_0$. Substituting function (16) into equation (14), we obtain

$$\frac{\partial f}{\partial t} + kw \left(v_1 \frac{\partial f}{\partial u_1} - u_1 \frac{\partial f}{\partial v_1} \right) = J(f), \quad (17)$$

where $u_1 = u \cos kz + v \sin kz$; $v_1 = -u \sin kz + v \cos kz$.

The variables u_1, v_1, w play the role of new velocities and t is the time. The dependence on the space coordinate z disappears. When $t = 0$ we can assign an initial function for equation (17)

$$f(t = 0, u_1, v_1, w) = f_0(u_1, v_1, w).$$

Let this initial function be such that

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 f du_1 dv_1 dw = \text{const}, \quad \text{and} \quad \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_1 f du_1 dv_1 dw = 0.$$

The initial distribution function when $t = 0$ will be

$$f(t=0, u_1, v_1, w) = f_0(u \cos kz + v \sin kz, -u \sin kz + v \cos kz, w).$$

Let us calculate the initial macroparameters: density, velocity components, and temperature:

$$n = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f_0 du dv dw = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f_0 du_1 dv_1 dw = n_0 = \text{const};$$

$$U = U_0 \cos kz; \quad V = U_0 \sin kz; \quad T = T_0 = \text{const},$$

where

$$U_0 = \frac{1}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 f_0 du_1 dv_1 dw = \text{const}.$$

We shall now show that in the motion process the density remains constant.

Integrating equation (17) with respect to velocities u_1, v_1, w between $-\infty$ and $+\infty$, we obtain $dn_1/dt = 0$, and consequently $n = n_1 = n_0$.

Multiplying equation (17) by w and integrating, we find that $dW/dt = 0$; /29
when taking the initial condition into account, this gives $W = 0$.

Successively multiplying equation (17) by the collision invariants u_1 , v_1 , $(u_1 - U_1)^2 + (v_1 - V_1)^2 + w^2$ and integrating between $-\infty$ and $+\infty$, we obtain the following moment equations:

$$\begin{aligned} \frac{dU_1}{dt} - \frac{k}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_1 w f du_1 dv_1 dw &= 0; \\ \frac{dV_1}{dt} + \frac{k}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 w f du_1 dv_1 dw &= 0; \\ \frac{dT_1}{dt} + \frac{km}{3\kappa n_0} \left[2U_1 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_1 w f du_1 dv_1 dw - 2V_1 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 w f du_1 dv_1 dw \right] &= 0, \end{aligned}$$

where $U_1 = \frac{1}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 f du_1 dv_1 dw$; $V_1 = \frac{1}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_1 f du_1 dv_1 dw$;

$$T_1 = \frac{2m}{3\kappa n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{(u_1 - U_1)^2 + (v_1 - V_1)^2 + w^2}{2} f du_1 dv_1 dw;$$

κ is the Boltzmann constant and m is the gas particle mass.

The third equation, with the first two taken into account, gives

$$\frac{d}{dt} \left[T_1 + \frac{m}{3\kappa} (U_1^2 + V_1^2) \right] = 0,$$

i.e.

$$T_1 + \frac{m}{3\kappa} (U_1^2 + V_1^2) = T_{10} + \frac{m}{3\kappa} U_{10}^2, \quad (18)$$

where T_{10} and U_{10}^2 are the T_1 and $U_1^2 + V_1^2$ values when $t = 0$. It can be shown that

$$U = U_1 \cos kz + V_1 \sin kz; \quad V = -U_1 \sin kz + V_1 \cos kz; \quad T = T_{10}.$$

From these relationships it follows that $U^2 + V^2 = U_1^2 + V_1^2$, i.e., the square of the velocity modulus is a function only of time. Relationship (18) may now be rewritten

$$n_0 \frac{3\kappa}{2} T + \frac{n_0 m (U^2 + V^2)}{2} = n_0 \frac{3\kappa}{2} T_0 + \frac{n_0 m U_0^2}{2}.$$

This equation expresses the law of conservation of energy for a unit volume of gas. The sum of the thermal energy of the gas and the kinetic energy of the macroscopic motion per unit volume is a constant.

The motion is interesting in another respect. It enables one to

determine the distribution function which is obtained as a solution when $t = \infty$.

Let us introduce the $H(t)$ function by means of the equation [5]:

$$H(t) = \iiint_{-\infty}^{+\infty} \ln f \, du_1 \, dv_1 \, dw.$$

In order to obtain an equation which defines the behavior of $H(t)$, we multiply equation (17) by $\ln(fe)$ and integrate with respect to the variables u_1 , v_1 , and w between $-\infty$ and $+\infty$. We then obtain

$$\frac{dH}{dt} = \iiint_{-\infty}^{+\infty} \ln(fe) J(f) \, du_1 \, dv_1 \, dw. \quad (19)$$

It is known that $\iiint_{-\infty}^{+\infty} \ln(fe) J(f) \, du_1 \, dv_1 \, dw \leq 0$.

Therefore $H(t)$ is a nonincreasing function.

We shall show that $H(t)$ has a lower limit and that the temperature $T_1 = 0$, for which we shall use the lemma proven in the work of Karleman [5, p. 27]:

Lemma. Let μ be the positive distribution of mass and Ψ be some continuous function.

Let us consider the class C of continuous functions $\varphi \geq 0$, which satisfy the conditions

$$\int_{\Omega} \varphi \, d\mu = A; \quad (20)$$

$$\int_{\Omega} \varphi \Psi^2 \, d\mu \leq B, \quad (21)$$

and let us assume that the function $\varphi_0 = ae^{-\alpha\Psi^2}$ exists, $\alpha > 0$, φ_0 an element of C is such that we have equality in (21). Then for all φ in C , the quantity $H(\varphi) = \int_{\Omega} \varphi \ln \varphi \, d\mu \geq H(\varphi_0)$ and the equality sign is valid only if $\varphi = \varphi_0$ in the region of the existence of μ .

In our case we can take the following as the equality of type (2)

$$\iiint_{-\infty}^{+\infty} f \, du_1 \, dv_1 \, dw = n_0$$

From relationship (18), it follows that the temperature

$$T_1(t) \leq T_0 + \frac{m}{3\kappa} U_0^2 = T_2.$$

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Therefore one can take $B = \frac{3\kappa n_0}{m} T_2$. The function Ψ should be taken in the form

$$\Psi = \sqrt{(u_1 - U_1)^2 + (v_1 - V_1)^2 + w^2} \cdot 3a\varphi_0. \text{ And}$$

the function φ_0 is taken to be $n_0 (m/2\pi\kappa T_2)^{3/2} \exp[-m\Psi^2/2\kappa T_2]$.

Then on the basis of the lemma, one can write

$$H(t) \geq H(\varphi_0) = \text{const.}$$

Thus we have established that $H(t)$ has a lower limit. Since $H(t)$ is non-increasing, the following inequality is valid:

$$H(t=0) \geq H(t) \geq H(\varphi_0). \quad (22)$$

Let us introduce the function $H(\varphi_1)$, constructed for

$$\varphi_1 = n_0 (m/2\pi\kappa T_1)^{3/2} \exp(-m\Psi^2/2\kappa T_1).$$

On the basis of the lemma, the following inequality must be fulfilled:

$$H(t) \geq H(\varphi_1) \geq H(\varphi_0). \quad (23)$$

It follows from (22) and (23) that $H(t=0) \geq H(\varphi_1) \geq H(\varphi_0)$. Having conducted calculations of $H(\varphi_1)$ and $H(\varphi_0)$ and substituting the inequalities into the latter we find

$$(mn_0^{2/3}/2\pi\kappa) \exp[-1 - 2H(t=0)/3n_0] \leq T_1(t) \leq T_2, \quad (24)$$

i.e., $T_1 \neq 0$. If the initial function is the local Maxwell distribution function, then the inequality (24) will acquire the following form

$$T_0 \leq T_1(t) \leq T_0 + \frac{m}{3\kappa} U_0^2,$$

i.e., the gas temperature cannot become lower than the initial temperature.

Since $H(t)$ is bounded below and is nonincreasing, then $\lim_{t \rightarrow \infty} dH/dt = 0$.

Therefore, from equation (19), it follows that

$$\int_{-\infty}^{+\infty} \ln f J(f) du_1 dv_1 dw = 0 \quad \text{when} \quad t = \infty.$$

The unique solution of this equation is a local Maxwell distribution function:

$$f_2 = n_0 (m/2\pi\kappa T_1)^{3/2} \exp \{-m[(u_1 - U_1)^2 + (v_1 - V_1)^2 + w^2]/2\kappa T_1\}.$$

The limits of the distribution function f when $t \rightarrow \infty$ must be function f_2 with some finite values U_1 , V_1 and T_1 , therefore $\lim_{t \rightarrow \infty} df/dt = 0$. Hence

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it follows that equation (17), when $t = \infty$, will acquire the following form

$$v_1 \frac{\partial f}{\partial u_1} - u_1 \frac{\partial f}{\partial v_1} = 0.$$

This equation must satisfy the limiting distribution function f_2 for u_1 , v_1 , and w values.

Substituting f_2 into the equation and requiring that f_2 be its solution, we obtain $u_1 v_1 - v_1 u_1 = 0$. Since this must be true for any u_1 and v_1 values, $U_1 = V_1 = 0$.

From equation (18) and the fact that when $t = \infty$, $U_1 = V_1 = 0$, it follows that $T_1(\infty) = T_2 = T_0 + (m/3\kappa)U_0^2$.

Thus, we found that the limiting distribution function in u , v , and w has the form:

$$f(t \rightarrow \infty, u, v, w) = n_0 (m/2\pi\kappa T_2)^{3/2} \exp[-m(u^2 + v^2 + w^2)/2\kappa T_2],$$

i.e., when $t \rightarrow \infty$, the gas is transformed into a quiescent state with an equilibrium distribution function and a temperature equal to T_2 .

3. Numerical Calculations of Spatially Uniform Motion on the Basis of a Model Kinetic Equation

For an approximate description of a gas flow whose distribution function is close to the local Maxwell distribution function, a model equation may be used instead of the Boltzmann equation [6].

For a second example of spatially uniform flow at $v = 5$ it has the form

$$\frac{\partial f}{\partial t} + w \frac{\partial f}{\partial z} = A n (f_0 - f), \quad (25)$$

where

$$f_0 = n(m/2\pi\kappa T)^{3/2} \exp\{-m[(u-U)^2 + (v-V)^2 + (w-W)^2]/2\kappa T\};$$

$A = \text{constant}$; n , T , U , V , W are defined through f from the known formulas.

The initial distribution function at $t = 0$ is

$$f(t=0, u, v, w) = n_0 \left(\frac{m}{2\pi\kappa T_0} \right)^{3/2} \exp \left\{ - \frac{m}{2\kappa T_0} [(v - U_0 \cos z)^2 + (v - U_0 \sin z)^2 + w^2] \right\}. \quad (26)$$

As before, it can be shown that $n = n_0$, $W = 0$, $T + \frac{2m}{3\kappa} \cdot \frac{U^2 + V^2}{2} = T_0 + \frac{m}{3\kappa} U_0^2$

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and when $t \rightarrow \infty$ the gas passes into a quiescent state with an equilibrium distribution function.

Let us seek macroscopic velocities U and V in the form

$$U = a(t)\cos z; \quad V = a(t)\sin z. \quad (27)$$

Substituting this macrovelocity distribution into equation (25) and integrating the equation taking initial condition (26) into account, we obtain

$$\begin{aligned} f = e^{-An_0 t} n_0 \left(\frac{m}{2\pi\kappa T_0} \right)^{3/2} \exp \left\{ -\frac{m}{2\kappa T_0} [(u - U_0 \cos(z - wt))^2 + (v - \right. \\ \left. - U_0 \sin(z - wt))^2 + w^2] \right\} + e^{-An_0 t} \int_0^t e^{An_0 \tau} An_0^2 \left(\frac{m}{2\pi\kappa T_0} \right)^{3/2} \exp \left\{ -\frac{m}{2\kappa T} \times \right. \\ \left. \times [(u - a \cos(z - wt + w\tau))^2 + (v - a \sin(z - wt + w\tau))^2 + w^2] \right\} d\tau, \end{aligned} \quad (28)$$

where $T(t)$ is expressed through the still random function $a(t)$ by the expression
$$T(t) = T_0 + \frac{mU_0^2}{3\kappa} - \frac{m}{3\kappa} a^2(t).$$
 In order to determine

the function $a(t)$ there are two relationships which distribution (28) must convert into an identity.

$$U = \frac{1}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u f du dv dw; \quad V = \frac{1}{n_0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v f du dv dw.$$

Substituting here the macrovelocity distribution (27) and function (28) and integrating we obtain a single condition imposed on $a(t)$:

$$\begin{aligned} a(t) = U_0 \exp(-An_0 t - t^2 2\kappa T_0 / 4m) + An_0 e^{-An_0 t} \int_0^t a(\tau) \exp \left\{ An_0 \tau - \right. \\ \left. - \frac{2\kappa}{m} (t - \tau)^2 \left[T_0 + \frac{mU_0^2}{3\kappa} - \frac{ma^2(\tau)}{3\kappa} \right] \right\} d\tau. \end{aligned}$$

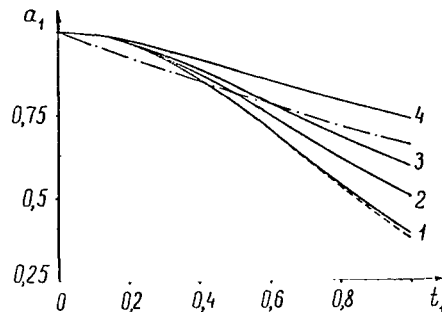
We reduce this equation to a dimensionless form, assuming $a(t) = U_0 a_1(t_1)$, $t = t_1 L_0 / U_0$ where L_0 is the characteristic dimension of the nonuniformity in the direction of the Oz axis:

$$\begin{aligned} a_1(t_1) = \exp(-\alpha t_1 - \beta t_1^2) + \alpha \int_0^{t_1} a_1(\tau) \exp \left\{ -\alpha(t_1 - \tau) - \right. \\ \left. - \beta \left[1 + \frac{(1 - a_1^2(\tau))}{6\beta} \right] (t_1 - \tau)^2 \right\} d\tau, \end{aligned}$$

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where $\alpha = 1/M_0 Kn_0 \sqrt{\frac{5\pi}{24}}$; $\beta = 3/10 M_0$; $M_0 = U_0 (3m/5 \pi T_0)^{1/2}$
 $Kn_0 = (8 \pi T_0 / \pi m)^{1/2} / L_0 An_0$.

The numerical solution of this equation was obtained by the iteration method on a "Strela" computer. The computation results are shown in the figure.



Changes in absolute velocity a_1 as a function of time; — calculated by the model equation; - - - calculated by the free molecular theory; — . — . calculated by the Navier-Stokes equation; 1 — $\beta = 1$,

$\alpha = 0,1$; 2 — $\beta = 1$, $\alpha = 1$; 3 — $\beta = 1$, $\alpha = 2$; 4 — $\beta = 1$, $\alpha = 5$

For comparison, the figure also gives the solution of this problem obtained by the Navier-Stokes equation. $a_1 = \sqrt{1 + 6\beta \exp[-(1 + 6\beta)t_1/3\alpha] / \sqrt{6\beta + \exp[-2(1 + 6\beta)t_1/3\alpha]}}$. Curves 1, 2, 3 and 4 correspond to the following values of the parameters: $\beta = 1$, $\alpha = 0,1$; $\beta = 1$, $\alpha = 1$; $\beta = 1$, $\alpha = 2$; $\beta = 1$, $\alpha = 5$ and are the plots of the dimensionless velocity modulus $a_1(t_1)$. The dashed curve represents the dependence $a_1(t_1)$ under free molecular flow conditions when $\beta=1$. It is apparent that curve 1 is close to the solution of the free molecular equation. An increase in parameter α with β remaining constant corresponds to a decrease in the Knudsen number, i.e. transition to the conditions of a continuous medium; however, at small t_1 values all curves approach the free molecular flow solution and are tangent to it at $t_1=0$. The curves behave this way because of the choice of the local Maxwell function as the initial distribution: this converts the collision integral to zero when $t_1=0$. Continuity the collision integral to remain small in some region of point $t_1 = 0$, and the gas flow remains close to the free molecular flow. For $\beta=1$ and

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$\alpha = 5$, a solution of the Navier-Stokes equation was constructed (dash-dot-dash curve), which differs significantly everywhere from the corresponding solution of the model equation (curve 4). This difference cannot be explained on the basis of the well-known characteristics of the model equation, since in the case being considered thermal conductivity is absent, Prandtl numbers are not involved, and the hydrodynamic equation obtained from the model equation by the Chapman-Enskog method coincides in the first approximation with the Navier-Stokes equation. Apparently, this difference is caused by the presence of "the temporary initial layer" [7] in the solution of the kinetic equation, in which the initial distribution function is converted to a function of the Navier-Stokes approximation [6]. The figure shows that the shift of the Navier-Stokes solution with time, equal in magnitude to the thickness of the initial layer, leads to a good agreement of solutions.

This example verifies the presence of an initial layer in the solution of the model equation.

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SOLUTION OF THE BOLTZMANN KINETIC EQUATION FOR THE RELAXATION OF A GAS MIXTURE

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Let us consider the temporal behavior of a quiescent mixture of two gases of different temperatures at the initial time $t = 0$, with spatially uniform distribution. /36

Physical considerations make it clear that when $t > 0$, heat transfer from one gas to the other takes place and the temperature difference between them begins to decrease.

This process of heating a cold gas by a hot gas will be investigated on the basis of the Boltzmann kinetic equation. The state of the first gas is described by a velocity distribution function of particles, $f(t, \vec{c})$, and that of the second gas by the velocity distribution function $F(t, \vec{c})$, where \vec{c} is the velocity vector.

We assume that the mixture is composed of absolutely hard smooth spheres with diameter σ_1 and mass m_1 for the first gas, and diameter σ_2 and mass m_2 for the second gas. We assume $m_1 \leq m_2$.

Let the density and the temperature of the first gas be n_1 and T_{10} and of the second gas be n_2 and T_{20} . The initial distribution functions for each gas is taken to be Maxwellian, i.e.,

$$\left. \begin{aligned} f_0(t=0, V) &= n_1 \left(\frac{m_1}{2\pi k T_{10}} \right)^{3/2} \exp \left[-\frac{m_1 V^2}{2k T_{10}} \right]; \\ F_0(t=0, V) &= n_2 \left(\frac{m_2}{2\pi k T_{20}} \right)^{3/2} \exp \left[-\frac{m_2 V^2}{2k T_{20}} \right], \end{aligned} \right\} \quad (1)$$

where k is the Boltzmann constant and V is the velocity modulus.

With such a choice of initial distribution functions, the solution of the Boltzmann kinetic equation will depend only on the velocity modulus V and the time t . In this case, the quintuple collision integrals in the Boltzmann equation are transformed to double integrals, as was done in [1]. /37

The transformed Boltzmann kinetic equations become

$$\left. \begin{aligned} \frac{\partial f(t, V)}{\partial t} &= J_{11}(f, f) + J_{12}(f, F); \\ \frac{\partial F(t, V)}{\partial t} &= J_{21}(F, f) + J_{22}(F, F), \end{aligned} \right\} \quad (2)$$

where

$$\begin{aligned} J_{11} &= 2\pi^2 \sigma_1^2 \int_0^V \int_{\sqrt{V^2-x^2}}^V f(t, x) f(t, y) \frac{4\sqrt{x^2+y^2-V^2}}{V} xy dy dx + \\ &+ 2\pi^2 \sigma_1^2 \left(\int_V^\infty f(t, x) 2x dx \right)^2 + 2\pi^2 \sigma_1^2 \int_0^V f(t, x) \frac{4x^2}{V} dx \times \\ &\times \int_V^\infty f(t, x) 2x dx - 2\pi^2 \sigma_1^2 f(t, V) \int_0^\infty f(t, x) \frac{(V+x)^3 - |V-x|^3}{3V} x dx; \\ J_{12} &= \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \frac{\pi^2}{V} \left(\frac{m_1 + m_2}{2m_2} \right)^2 \left\{ \int_0^\infty \int_{y_1}^{y_2} f(t, x) F(t, y) \left[(x+V) - \right. \right. \\ &- \left. \frac{m_2}{m_1} \left| y - \left(y^2 + \frac{m_1}{m_2} (x^2 - V^2) \right)^{1/2} \right| \right] 1xy dy dx + \int_0^\infty \int_{y_2}^\infty f(t, x) F(t, y) (x+V - \\ &- |x-V|) 1xy dy dx + \int_{x_1}^{x_2} \int_{y_0}^{y_1} f(t, x) F(t, y) \frac{m_2}{m_1} 2 \left(y^2 + \frac{m_1}{m_2} (x^2 - V^2) \right)^{1/2} \times \\ &\times 1xy dy dx + \int_V^{x_2} \int_0^{y_1} f(t, x) F(t, y) 2 \frac{m_2}{m_1} 1xy^2 dy dx \left. \right\} - \\ &\left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 2\pi^2 f(t, V) \int_0^\infty F(t, y) \frac{(V+y)^3 - |V-y|^3}{3V} y dy; \\ J_{22} &= 2\pi^2 \sigma_2^2 \int_0^V \int_{\sqrt{V^2-x^2}}^V F(t, x) F(t, y) \frac{4\sqrt{x^2+y^2-V^2}}{V} xy dy dx + \\ &+ 2\pi^2 \sigma_2^2 \left(\int_V^\infty F(t, x) 2x dx \right)^2 + 2\pi^2 \sigma_2^2 \int_0^V F(t, x) \frac{4x^2}{V} dx \times \end{aligned}$$

$$\begin{aligned}
& \times \int_V^\infty F(t, x) 2x dx - 2\pi^2 \sigma_2^2 F(t, V) \int_0^\infty F(t, x) \frac{(V+x)^3 - |V-x|^3}{3V} x dx; \\
J_{21}(F, f) = & \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \frac{\pi^2}{V} \left(\frac{m_1 + m_2}{2m_1} \right)^2 \left\{ \int_0^\infty \int_{y_1 m_2 / m_1}^{y_2 m_2 / m_1} f(t, y) F(t, x) \times \right. \\
& \times \left[\frac{m_1}{m_2} \left(y + \left(y^2 + \frac{m_2}{m_1} (x^2 - V^2) \right)^{1/2} \right) - |V - x| \right] 4xy dy dx + \\
& + \int_0^\infty \int_{y_2 m_2 / m_1}^\infty f(t, y) F(t, x) (V + x - |V - x|) 4xy dy dx + \\
& + \int_V^{x_2} \int_0^{y_1 m_2 / m_1} f(t, y) F(t, x) 2 \frac{m_1}{m_2} y 4xy dy dx + \\
& + \int_V^\infty \int_{y_0 m_2 / m_1}^{y_1 m_2 / m_1} f(t, y) F(t, x) \frac{m_1}{m_2} \left(y^2 + \frac{m_2}{m_1} (x^2 - V^2) \right)^{1/2} 8xy dy dx \Big\} - \\
& - \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 2\pi^2 F(t, V) \int_0^\infty f(t, y) \frac{(V+y)^3 - |V-y|^3}{3V} y dy,
\end{aligned}$$

where

$$\begin{aligned}
x_1 = \frac{m_2 - m_1}{m_2 + m_1} V; \quad x_2 = \frac{m_2 + m_1}{m_2 - m_1} V; \quad y_0 = \left[\frac{m_1}{m_2} (V^2 - x^2) \right]^{1/2}; \\
y_1 = \frac{1}{2} |(V-x) + (V+x)m_1/m_2|; \quad y_2 = \frac{1}{2} |(V+x) + (V-x)m_1/m_2|.
\end{aligned}$$

In order to determine the distribution functions $f(t, V)$ and $F(t, V)$, it is necessary to solve the Cauchy problem for the system of equations (2) with initial conditions (1).

Below we will give a numerical solution for this problem.

Let us first note certain properties of the solution to be found which can be established prior to solving the problem.

From the conservation equations it follows that in the relaxation process the densities of the number of particles, n_1 , n_2 and the sum of the gas temperatures, $T_1 + T_2$, will remain constant.

It follows from the Boltzmann H-theorem that when $t \rightarrow \infty$, the distribution functions f and F become [2]:

$$f = n_1 \left(\frac{m_1}{2\pi k T_\infty} \right)^{3/2} \exp \left(- \frac{m_1 V^2}{2k T_\infty} \right); \quad \text{39}$$

$$F = n_2 \left(\frac{m_2}{2\pi k T_\infty} \right)^{3/2} \exp \left(- \frac{m_2 V^2}{2k T_\infty} \right),$$

where $T_\infty = (T_{10} + T_{20})/2$ is the temperature of the mixture at equilibrium.

It is apparent that when $t \rightarrow \infty$

$$T_1(t) \rightarrow T_\infty \quad \text{and} \quad T_2(t) \rightarrow T_\infty.$$

The above indicated properties were used for controlling the count.

In finding the numerical solution of the equations, it is convenient to convert to dimensionless variables by means of the following equations

$$t = \tau_1 t'; \quad V = c_2 V';$$

$$f = n_1 \left(\frac{m_1}{2\pi k T_\infty} \right)^{3/2} f'; \quad F = n_2 \left(\frac{m_2}{2\pi k T_\infty} \right)^{3/2} F',$$

where t' , V' , f' , and F' are dimensionless quantities and their coefficients are characteristic scaling factors; τ_1 was selected to equal the average time between successive collisions of particles of type-one gas when the mixture is at equilibrium:

$$\tau_1 = \frac{1}{4} \left(\frac{m_1}{\pi k T_\infty} \right)^{1/2} \left[n_1 \sigma_1^2 + n_2 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \left(\frac{m_1 + m_2}{2m_2} \right)^{1/2} \right]^{-1};$$

$c_2 = (3kT_\infty/m_2)$ is the mean thermal velocity of gas particles of the second type when $t = \infty$.

The first time step, allowing movement away from the initial distribution functions, is carried out using the Euler method:

$$f'(\Delta t', V') = f'_0(V') + J_{11}(f'_0, f'_0)\Delta t' + J_{12}(f'_0, F'_0)\Delta t';$$

$$F'(\Delta t', V') = F'_0(V') + J_{22}(F'_0, F'_0)\Delta t' + J_{21}(F'_0, f'_0)\Delta t'.$$

Subsequently computations are by the modified Euler formula:

$$\begin{aligned} f'(t'_{k+1}, V') &= f'(t'_{k-1}, V') + J_{11} [f'(t'_k, V'), f'(t'_k, V')] 2\Delta t' + \\ &\quad + J_{12} [f'(t'_k, V'), F'(t'_k, V')] 2\Delta t'; \\ F'(t'_{k+1}, V') &= F'(t'_{k-1}, V') + J_{22} [F'(t'_k, V'), F'(t'_k, V')] 2\Delta t' + \\ &\quad + J_{21} [F'(t'_k, V'), f'(t'_k, V')] 2\Delta t'. \end{aligned}$$

The double integral is evaluated by repeated computation of single integrals. The latter were evaluated by the trapezium method. /40

From the found values of the f' and F' distribution functions, the dimensionless temperatures T_1' and T_2' were calculated by formulas

$$\begin{aligned} T_1' &= 4\pi \left(\frac{m_1}{2} \right)^{5/2} \left(\frac{3}{2\pi} \right)^{3/2} \int_0^\infty f' V'^4 dV'; \quad T_2' = 4\pi \left(\frac{3}{2\pi} \right)^{3/2} \int_0^\infty F' V'^4 dV' \\ (T_1 &= T_\infty T_1', \quad T_2 = T_\infty T_2'). \end{aligned}$$

These calculations were conducted on the BESM-6 electronic digital computer at the Computer Center of the Academy of Sciences of the USSR. A mixture consisting of methane and argon was taken for specific calculations.

The type-one gas was methane, the type-two gas argon. The initial argon temperature was 10,000°K, while that of methane was 300°K.

The gas densities were

$$n_1 = n_2 = 10^{18} \text{ cm}^{-3}.$$

At equilibrium the mean time between the collisions of methane particles was found to be $\tau_1 \approx 0.34 \times 10^{-9}$ sec. The solid curve in Figure 1 shows the uniform increase in methane temperature T' resulting from its heating by argon.

After a period equivalent to seven collision times, the methane temperature differs from the equilibrium value by only 9%, i.e. one can say that in this example the temperature relaxation time is

of the order of 7-8 collisions.

Figure 2 shows graphs of the $f'V'^2$ function for various times. The subscript on the function designates the time to which the curve refers.

Figure 3 shows the changes in the $F'V'^2$ function for argon. The solution obtained for the problem allows a certain evaluation of the accuracy of the approximate method for solving the Boltzmann kinetic equation.

The problem of the relaxation of a mixture of gases was solved in [3, 4] by the statistical Monte Carlo method, in which the motion of a large number of molecules is observed simultaneously. The essence of that method has been described in detail in the indicated references.

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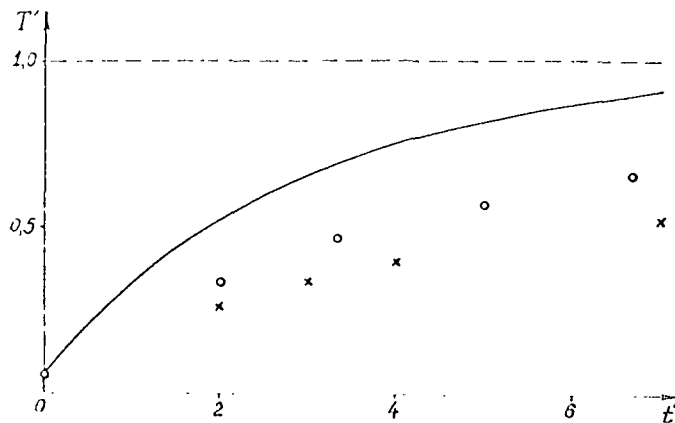


Figure 1. Graph representing temperature increase of methane T' as a function of time.

Our calculations were made for the same specific gases and with the same initial distribution functions as in [3, 4]. Their results were recalculated to our dimensionless variables and plotted for various time intervals as circles and x's in Figure 1. The x's apply to data in [3], while the circles represent the data in [4].

The graph shows that the results obtained by the authors

of [3, 4] differ from the precise solution by an average of 30%.

Comparing the results in [3] and [4] over a range of methane temperatures shows poor agreement. In [3] a periodic, nonuniform increase in methane temperature was discovered. This is absent in the solution which we obtained.

Remarks. In the discussion with one of the authors of references [3, 4], Yu. G. Malama, it was found that in these articles the densities of argon and methane gases were erroneously given as 10^{18} cm^{-3} . The correct values are $0.5 \times 10^{18} \text{ cm}^{-3}$. This leads to changes in the time scale by a factor of two. For comparison of the data of [4] with our results with respect to the methane temperatures and taking into account the above-mentioned discrepancy, it is necessary to reduce the abscissa of the circles in Figure 1 by a factor of two. /43 Such a comparison yields satisfactory agreement of results.

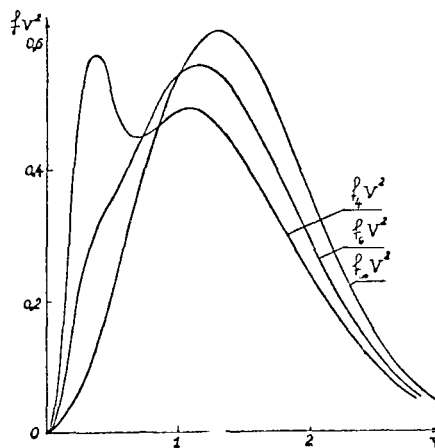
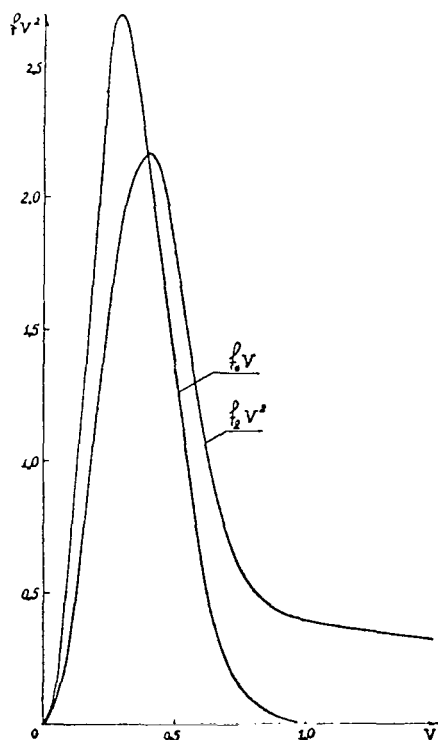


Figure 2. Graphs of the fV^2 function for different times. The subscripts on the functions designate the time to which each curve refers.

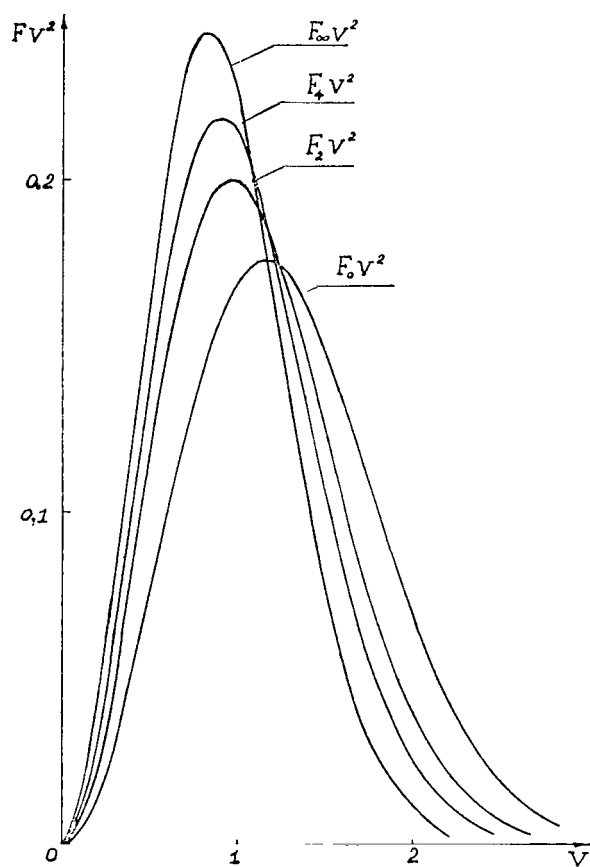


Figure 3. Dependence of the FV^2 function on the magnitude of V for argon. The subscripts on the function F designate the times to which each curve refers ($t_1 = 0$, $t_1 = 2$, $t_1 = 4$, $t_1 = \infty$).

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A METHOD FOR DIRECT NUMERICAL INTEGRATION
OF THE BOLTZMANN EQUATION

F. G. Cheremisin

1. Principal Difficulties in Numerical Solution
of the Boltzmann Equation

A rigorous formulation of problems in the flow of rarefied gases is provided by the Boltzmann kinetic equation, which permits description of significant changes in flow properties at distances on the order of the mean free path or during a time comparable to the mean time between molecular collisions.

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The Boltzmann equation introduces a molecular velocity distribution function $f(\vec{\xi}, \vec{x}, t)$, which is determined in the so-called "phase space" of a molecule $(\vec{\xi}, \vec{x})$ and it is also time dependent. The hydrodynamic characteristics of flow (density, average velocity, temperature, momentum and energy fluxes) are all determined from the found distribution function as the corresponding means over velocity subspace.

As in ordinary hydrodynamics, these quantities sufficiently well characterize the flow, and their determination is of fundamental interest.

The uniqueness and the difficulty of the problem, however, lies in the fact that it is not possible to construct a closed system of equations for the hydrodynamic quantities, and their determination requires the preliminary calculation of the distribution function, i.e., it requires a significantly more detailed description. After such a description is achieved (the distribution function is found), "excess" information is eliminated by calculating the corresponding mean quantities.

Naturally, one attempts to formulate numerical solution of the Boltzmann equation in such a manner that it contains a minimum amount of excess information at the distribution function level. The desired distribution function \tilde{f} must satisfy the following requirements:

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$$\left. \begin{aligned} |\int \Psi_i (\tilde{f} - f) d\vec{\xi}| &< \epsilon_i; \\ |\int \vec{\xi} \Psi_i (\tilde{f} - f) d\vec{\xi}| &< \epsilon'_i, \end{aligned} \right\} \quad (1)$$

where f is the precise value of the distribution function; $\Psi_i = \{1, \vec{\xi}, \xi^2\}$ are molecular collision invariants; the parameters ϵ_i, ϵ'_i stipulate the required accuracy in calculating the hydrodynamic quantities.

Inequalities (1) determine how close, on the average, the computed distribution function is to the true value. These conditions can be satisfied simultaneously if the distribution functions are computed at each point in physical space (\vec{x}, t) with statistical accuracy, i.e., so that the computed values contain the statistical error ϵ_0 , randomly distributed around $\epsilon_0 \approx 0$.

The accurate calculation of the distribution function at each point in phase space requires a tremendous number of operations, due to the necessity of solving five-fold quadratures in the collision integral. The sufficiency requirements on the average allow the calculations to be carried out with only statistical accuracy and significantly reduce the number of necessary calculations.

The second principal difficulty, also associated with the necessity of detailed description, is the sharp increase in the necessary machine memory. In even the simplest one-dimensional steady-state gas motions, the problem at the distribution function level becomes at least three-dimensional, and the magnitude of the distribution function as a rule changes significantly over all three variables.

Evaluations show that in order to store data on the distribution functions at the necessary number of points in phase space, the operational memory of a modern electronic digital computer is insufficient.

2. Scheme for Integral Iterations

Let us construct an algorithm involving successive iterations of the Boltzmann equation which does not require storage of each step of the new

distribution function.

The Boltzmann equation may be written in the form

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$$\begin{aligned} \frac{\partial f}{\partial t} + \vec{\xi} \cdot \frac{\partial f}{\partial \vec{x}} + \nu f &= N; \\ \nu &= \frac{1}{m} \int B(0, \vec{\xi}, \vec{\xi}_1) f_1 d\omega d\vec{\xi}_1; \\ N &= \frac{1}{m} \int B(0, \vec{\xi}, \vec{\xi}_1) f' f'_1 d\omega d\vec{\xi}_1, \end{aligned} \quad (2)$$

where $f_1 \equiv f(\vec{\xi}_1)$; $f' \equiv f(\vec{\xi}')$; $d\omega = \sin \theta d\theta d\epsilon$; $\vec{\xi}' = \vec{\xi}'(\theta, \epsilon, \vec{\xi}, \vec{\xi}_1)$; $\vec{\xi}'_1 = \vec{\xi}'_1(\theta, \epsilon, \vec{\xi}, \vec{\xi}_1)$; and θ and ϵ are collision parameters.

In equation (2) the collision integral is in two parts, the first of which, νf , describes the decrease in the distribution function as a result of collisions of an isolated group of molecules with all others, the second part of the integral, on the right, gives the increase in the number of molecules in the selected element of phase volume resulting from molecular collisions in all the remaining space. Strictly speaking, such a subdivision of the Boltzmann integral is admissible only when molecular interacting has a finite radius. The rapid decrease of the intermolecular potential for neutral gases with distance justifies limiting of the interaction radius. During numerical integration the limitation of the region of changes of the impact parameter (with subsequent testing of the insignificance of such limitations) is necessary.

The following iteration method for the solution of equation (2) appears desirable:

$$\frac{\partial f^{(n)}}{\partial t} + \vec{\xi} \cdot \frac{\partial f^{(n)}}{\partial \vec{x}} + \nu^{(n-1)} f^{(n)} = N^{(n-1)}, \quad (3)$$

where

$$\begin{aligned} \nu^{(n-1)} &= \frac{1}{m} \int B f_1^{(n-1)} d\omega d\vec{\xi}_1; \\ N^{(n-1)} &= \frac{1}{m} \int B f^{(n-1)} f_1^{(n-1)} d\omega d\vec{\xi}_1 \end{aligned}$$

etc.

The convergence of this process, which was used for proving the theorem of existence of solutions for the Boltzmann equation, was established only for spatially homogeneous flow and for "sufficiently small" $t - t_0$ values, where t_0 is the initial moment of time in the general case. However, one would expect convergence to take place at any $t - t_0$ values, at least if the zero approximation has been selected successfully.

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Integrating (3), we obtain

$$f^{(n)}(\vec{\xi}, \vec{x}, t) = f(\vec{\xi}, \vec{x}_0, t_0) \exp \left\{ - \int_{t_0}^t v^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) dt_1 \right\} + \int_{t_0}^t N^{(n-1)}(\vec{\xi}, \vec{x}_\tau, \tau) \exp \left\{ - \int_{\tau}^t v^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) dt_1 \right\} d\tau, \quad (4)$$

where $\vec{x}_1 = \vec{x} - \vec{\xi}(t - t_1)$; $\vec{x}_0 = \vec{x} - \vec{\xi}(t - t_0)$; $\vec{x}_\tau = \vec{x} - \vec{\xi}(t - \tau)$;

$$v^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) = \frac{1}{m} \int B f^{(n-1)}(\vec{\xi}_1, \vec{x}_1, t_1) d\omega d\vec{\xi}_1; \quad (5)$$

$$N^{(n-1)}(\vec{\xi}, \vec{x}_\tau, \tau) = \frac{1}{m} \int B f^{(n-1)}(\vec{\xi}', \vec{x}_\tau, \tau) f^{(n-1)}(\vec{\xi}_1, \vec{x}_\tau, \tau) d\omega d\vec{\xi}_1. \quad (6)$$

In turn

$$f^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) = f(\vec{\xi}_1, \vec{x}_{01}, t_{01}) \times \exp \left\{ - \int_{t_0}^t v^{(n-2)}(\vec{\xi}_1, \vec{x}_2, t_2) d\tau_2 + \dots \right\}, \quad (7)$$

where $\vec{x}_2 = \vec{x}_1 - \vec{\xi}_1(t_1 - t_2)$; $\vec{x}_{01} = \vec{x}_1 - \vec{\xi}_1(t_1 - t_{01})$, ... etc.

From this we see that the solution of equations (4)-(7) is written in a form which allows introduction of both initial and boundary conditions.

If one considers the problem with initial condition $t = t_0$, then

$$f(\vec{\xi}, \vec{x}_0, t_0) = \varphi(\vec{\xi}, \vec{x} - \vec{\xi}(t - t_0)).$$

For a problem with the assigned function at the boundary, one must assume

$$f(\vec{\xi}, \vec{x}_0, t_0) = \varphi \left(\vec{\xi}, \vec{x}_s, t - \frac{|\vec{x} - \vec{x}_s|}{|\vec{\xi}|} \right),$$

where \vec{x}_s is the intersection of the ray drawn from point \vec{x} in the direction of $-\vec{\xi}$ with the boundary surface. One can also have a mixed problem, when the distribution function is stipulated on certain surfaces and at certain specified initial moments of time. In this case the initial data can be referred to $t = 0$, and one can consider $f(\vec{\xi}, \vec{x}_0, t_0)$ to be a function stipulated on the boundary or an initial value, depending on whether the characteristic originating at point x in the $-\vec{\xi}$ direction intersects the boundary surface at $t > 0$ or enters the region of initial data at $t = 0$. /49

Let us assume that the $(n-1)$ th iteration has been performed and $f^{(n-1)}$ is a known function. Let us seek $f^{(n)}(\vec{\xi}, \vec{x}, t)$ at a designated phase point $(\vec{\xi}, \vec{x})$ at time t . For this purpose it is necessary to calculate $v^{(n-1)}(\vec{\xi}, \vec{x}, t)$ and $N^{(n-1)}(\vec{\xi}, \vec{x}, t)$ at a number of points (t_1, \vec{x}_1) , where $\vec{x}_1 = \vec{x} - \vec{\xi}(t - t_1)$. Let us calculate these integrals at each point (t_1, \vec{x}_1) by random sampling. For this purpose we shall take a set of random numbers $(\vec{\xi}_1, \theta_1, \epsilon_1)$, calculate $(\vec{\xi}_1, \theta_1, \epsilon_1)$ for each, calculate the values $\vec{\xi}'$ for each assigned value $\vec{\xi}_1$ and $\vec{\xi}_1'$, and then find the corresponding values of $f^{(n-1)}(\vec{\xi}_1, \vec{x}_1, t_1)$, $f^{(n-1)}(\vec{\xi}_1', \vec{x}_1, \tau)$ and $f_1^{(n-1)}(\vec{\xi}_1', \vec{x}_1, \tau)$. Integrals (5) and (6) are the sums of the integrands at different points $(\vec{\xi}_1, \theta, \epsilon)$. In turn the values of $f^{(n-1)}$ at the required points $(\vec{\xi}_1, \vec{x}_1, t_1)$, $(\vec{\xi}_1', \vec{x}_1, \tau)$ and $(\vec{\xi}_1', \vec{x}_1, \tau)$ must be calculated in the same manner from the $f^{(n-2)}(\vec{\xi}_2, \vec{x}_2, t_2)$ values etc.

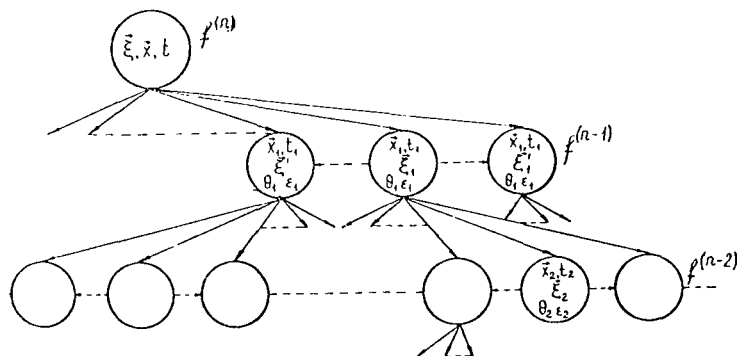


Figure 1. The sequential approximations scheme.

The calculation scheme is represented in Figure 1; the points at which the successive iterations must be computed are indicated. One can preliminarily sample (from top to bottom) a sequence of random numbers which characterizes each apex of the diagram, and then carry out successive iterations (from bottom to top). However, storing all the sets of random numbers is no less difficult a problem than storing the distribution functions.

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Let us join each three apices connected in Figure 1 by dashed lines into a single apex A_{n-1} , A_{n-2} , The obtained "graph," known as a "tree" (Figure 2), is characteristic in that each of its apices A_{k-1} is determined only by a single preceding A_k . This situation plays an important role, since storage of the whole tree in the memory in advance is not necessary, but only a single branch represented in Figure 2.

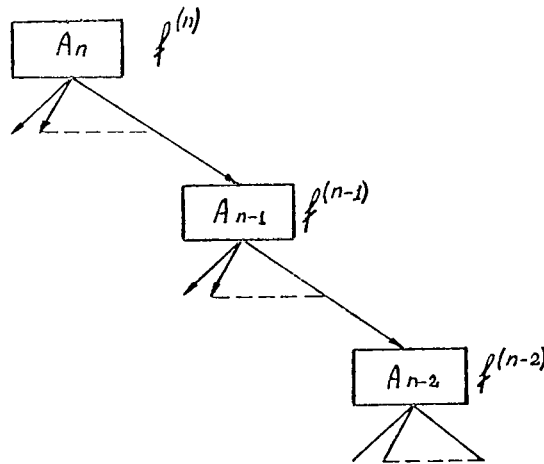


Figure 2. Iteration tree for the Boltzmann equation.

For the assigned value of the root A , consider the random numbers which define one of the apices A_{n-1} ; for this apex define one of the apices A_{n-2} , etc., until A_1 is reached; take only as many values of A_0 as are necessary for the calculation of $f^{(1)}$ at apex A_1 . Then, changing the value of the random vector which defines A_1 , and taking a new set of A_0 , calculate the values of $f^{(1)}$ at the new apex A_1' . Repeat this process

until enough values of $f^{(1)}$ at apexes A_1, A_1', \dots , have been acquired to calculate the second iteration $f^{(2)}$ at one of the apexes A_2 ; then similarly calculate $f^{(2)}$ in apex A_2' , etc., until A_n is reached.

It can easily be shown that memory space problems do not arise in practice for any number of iterations ("generations" of the tree, Figure 2), since the zero iteration can always be stipulated in analytical form. However, the volume of calculations avalanches with each new iteration. A significant reduction in calculations can be achieved by using statistical considerations, similar to those which were expressed in Section 1 of this chapter, in conducting subsequent iterations. /51

Requirements similar to (1) must be imposed for integrals containing $f^{(n-1)}$ and which enter into the definition of $f^{(n)}$. It is important to note that smoothing of $f^{(n-1)}$ occurs not only at each point (\vec{x}, t) , but also along the characteristic.

In carrying out n iterations, $n-1$ levels arise, each of which results in the smoothing of the previous iteration. Finally, the obtained function of $f^{(n)}$ is integrated for obtaining the hydrodynamic quantities.

This computation method may be used for finding accurate $f^{(n)}$ values at a small number of phase points (construction of distribution function profiles, etc.). In this case $f^{(n)}$ is calculated through $f^{(n-1)}$ over a sufficiently large number of sets of random numbers, and all previous iterations are performed as described above. The best calculation conditions are chosen and calculations are checked by changing the number of trials in each generation of the iteration tree.

3. Stochastic Boundary Conditions

In Section 2 we considered the problem with assigned initial or boundary functions. In calculating the hydrodynamic flow of rarefied gas around various bodies, the so-called stochastic boundary condition is frequently used; this describes the incident and the reflected flow of molecules from a surface element:

$$\int_{(\vec{\eta}, \vec{n}) > 0} (\xi, x_s, t) = \int_{(\vec{\eta}, \vec{n}) < 0} K(\vec{\xi}, \vec{\eta}) f(\vec{\eta}, \vec{x}_s, t) d\vec{\eta}, \quad (8)$$

where \vec{n} is the external normal to the surface element. The scattering nucleus $K(\vec{\xi}, \vec{\eta})$ characterizes the properties of the reflecting surface and may contain such parameters as temperature and average velocity, describing the surface state, and also various accommodation coefficients, which characterize its structure. One can take into account the partial accommodation of incident molecules if one assumes that the fraction α of the incident beam undergoes mirror reflection, while the remainder leaves the wall with a Maxwellian distribution corresponding to some new values of mean temperature and mean velocity. In this case [1]:

$$K(\vec{\xi}, \vec{\eta}) = \alpha \delta[(\vec{n} \cdot \vec{\xi}) + (\vec{n} \cdot \vec{\eta})] + (1 - \alpha) \frac{(\vec{n} \cdot \vec{\eta})}{2\pi T_0} \exp\left\{-\frac{(\xi - u)^2}{2T_0}\right\},$$

where $\delta(y)$ is the delta function.

Boundary condition (8) may be included in the scheme of Section 2 by isolating the cone of influence of the body Ω at the point (\vec{x}, t) (Figure 3).

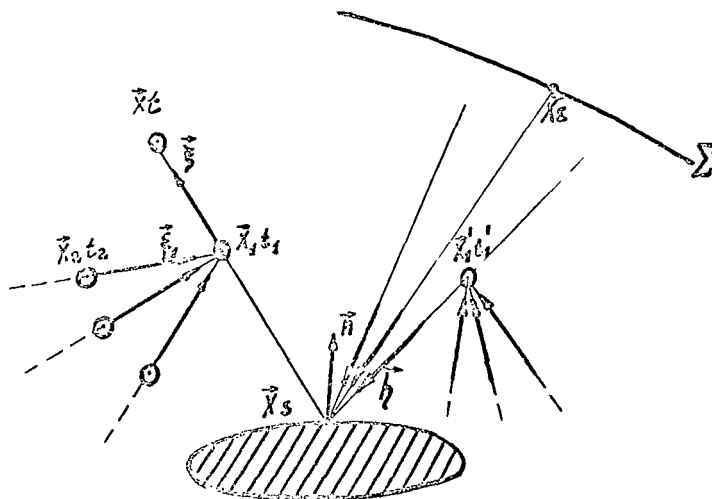


Figure 3. Calculation scheme for stochastic boundary condition.

The conditions at infinity may be replaced in practical calculations by assigning boundary conditions $f(\vec{\xi}, \vec{x}_\Sigma, t) = f_\infty(\vec{\xi}, t)$ on some limiting surface Σ . We obtain

$$f^{(n)}_{\vec{\xi} \in \Omega}(\vec{\xi}, \vec{x}, t) = f^{(n)}(\vec{\xi}, \vec{x}_s, t) \exp \left\{ - \int_{t_0}^t v^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) dt_1 \right\} + \dots; \quad (9)$$

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$$f^{(n)}_{\vec{\xi} \in \Omega}(\vec{\xi}, \vec{x}, t) = f_\infty(\vec{\xi}, t_0) \exp \left\{ - \int_{t_0}^t v^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) dt_1 \right\} + \dots. \quad (10)$$

Substituting into equation (9) the value

$$f^{(n)}_{\substack{\vec{\xi} \in \Omega \\ (\vec{\xi} \cdot \vec{n}) > 0}}(\vec{\xi}, \vec{x}_s, t_0) = \int_{\substack{\vec{\eta} \in \Omega \\ (\vec{\eta} \cdot \vec{n}) < 0}} K(\vec{\xi}, \vec{\eta}) f^{(n)}(\vec{\eta}, \vec{x}_s, t_0) d\vec{\eta}. \quad (11)$$

For simplicity we can consider that $\vec{\eta} \in \Omega$ (this is always valid for convex surfaces). Then $f^{(n)}(\vec{\eta}, \vec{x}_s, t_0)$ can be described by formula (10), in which one should replace $\vec{\xi} \rightarrow \vec{\eta}$, $\vec{x} \rightarrow \vec{x}_s$, $t \rightarrow t_0$.

We shall obtain

$$f^{(n)}_{\vec{\xi} \in \Omega}(\vec{\xi}, \vec{x}, t) = \exp \left\{ - \int_{t_0}^t v^{(n-1)}(\vec{\xi}, \vec{x}_1, t_1) dt_1 \right\} \int K(\vec{\xi}, \vec{\eta}) \times \left[f_\infty(\vec{\eta}, t_0) \exp \left\{ - \int_{t'_0}^t v^{(n-1)}(\vec{\eta}, \vec{x}'_1, t'_1) dt'_1 + \dots \right\} d\vec{\eta} + \dots \right]. \quad (12)$$

Formulas (10) and (12) express the function $f^{(n)}(\vec{\xi}, \vec{x}, t)$ at any values of the vector $\vec{\xi}$ through the values of the distribution function at the outer boundary and the $(n-1)$ th approximation. Relationships, analogous to (9)-(12), must be written for $f^{(n-1)}$, $f^{(n-2)}$, ..., etc.

Each step during additional integration for $\vec{\eta}$ in (12) increases the number of calculations for $\vec{\xi} \in \Omega$ by as many values as the required $\vec{\eta}$ number for calculation of the integral containing the kernel $K(\vec{\xi}, \vec{\eta})$. An exception is the case of pure mirror reflection: here a single vector corresponds to one $\vec{\eta}$ value and there is no significant increase in the volume of calculations.

Figure 3 explains the calculation scheme for stochastic boundary conditions on the body. It is obvious that the construction of one tree with a root at the assigned point $(\vec{\xi}, \vec{x}, t)$ and $\vec{\xi} \in \Omega$ requires additional construction of several trees, having a common root at the point $\vec{x}_s(\vec{\xi}, t)$. This, apparently, is valid for each apex $(\vec{\xi}_i, \vec{x}_i, t_i)$ of the initial tree, and also for the apexes of the trees which originate at points \vec{x}_s , if $\vec{\xi}_i \in \Omega$.

As in the case of assigned boundaries or initial functions, memory problems do not arise when using stochastic boundary conditions.

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4. Choosing the Zero Approximation

Since an increase in the number of iterations leads to a significant increase in the volume of calculations, the apt choice of the zero approximation is important.

If the flow of gas is close to the hydrodynamic limit ($K_n < 1$), the Maxwell distribution function may be selected as the zero approximation:

$$f_0 = n_0 \left(\frac{m}{2\pi T_0} \right)^{3/2} \exp \left\{ - \frac{m(\vec{\xi} - \vec{v}_0)^2}{2T_0} \right\}. \quad (13)$$

The parameters $n(\vec{x}, t)$, $T_0(\vec{x}, t)$, $\vec{v}_0(\vec{x}, t)$ which enter into equation (13) must be determined a priori from the hydrodynamic equations. Then integrals $v^{(0)}$ and $N^{(0)}$ can be expressed as functions of n_0 , T_0 , \vec{v}_0 and $\vec{\xi}$. The calculation of the first iteration will require a significantly smaller number of elementary operations. Since a large proportion of the calculations are made in the first iteration, this will significantly reduce the total volume of calculations. In the case of large Knudsen numbers, the free molecular solution can be used as the zero approximation:

$$f(\vec{\xi}, \vec{x}, t) = \varphi(\vec{\xi}, \vec{x} - \vec{\xi}(t - t_0), t_0).$$

In the intermediate region, one of the "rough" solutions of the Boltzmann equation can be used (for example, the Mott-Smith solution for shock waves) or the solution of the corresponding problem of the so-called "relaxation" kinetic equation, in which the Boltzmann integral is replaced by a simplified

expression $J = -v_r(n, T, \vec{u})(f - f_0)$.

The relaxation equation may also be used in order to reduce the volume of calculations for conducting the first iteration by the above method. Then, if we consider the values $n_0(\vec{x}, t)$, $T_0(\vec{x}, t)$, $\vec{v}_0(\vec{x}, t)$ in the zero approximation to be stipulated we obtain

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$$f^{(1)}(\vec{\xi}, \vec{x}, t) = f(\vec{\xi}, \vec{x}_0, t_0) \exp \left\{ - \int_{t_0}^t v_r dt_1 \right\} + \int_{t_0}^t v_r f_0(\vec{\xi}, \vec{x}_\tau, \tau) \exp \left\{ - \int_{\tau}^t v_r dt_1 \right\} d\tau.$$

We can then proceed with the calculation of $f_2(\vec{\xi}_{n-2}, \vec{x}_{n-2}, t_{n-2})$, etc., now according to the precise Boltzmann equation.

5. Solution of the Problem of Homogeneous Gas Relaxation

As an example of application of the above considerations, we shall cite a solution of the problem of the homogeneous relaxation of gas consisting of solid elastic spheres (Cauchy problem for the Boltzmann equation).

The Boltzmann equation is written in the form [2]

$$\frac{\partial f(\vec{\xi}, t)}{\partial t} = J[f]; \quad (14)$$

$$J[f] = \frac{\sigma^2}{2} \iiint_{-\infty}^{\infty} \int_0^{2\pi} \int_0^{\pi} [f(t, \xi', \eta', \zeta') f(t, \xi'_1, \eta'_1, \zeta'_1) - f(t, \xi, \eta, \zeta) f(t, \xi_1, \eta_1, \zeta_1)] |q| \sin \theta d\theta d\varphi d\xi_1 d\eta_1 d\zeta_1, \quad (15)$$

where $\xi, \eta, \zeta, \xi_1, \eta_1, \zeta_1, \dots$ are components of the vectors $\vec{\xi}, \vec{\xi}_1, \dots$;

$$\left. \begin{aligned} \xi' &= \xi + lq; & \eta' &= \eta + mq; & \zeta' &= \zeta + nq; \\ \xi'_1 &= \xi - lq; & \eta'_1 &= \eta - mq; & \zeta'_1 &= \zeta - nq; \\ q &= l(\xi_1 - \xi) + m(\eta_1 - \eta) + n(\zeta_1 - \zeta); \\ l &= \cos \theta; & m &= \sin \theta \cos \varphi; & n &= \sin \theta \sin \varphi. \end{aligned} \right\} \quad (16)$$

When $t = 0$ the initial value is stipulated for equation (14):

$$f(\vec{\xi}, 0) = \varphi_0(\vec{\xi}). \quad (17)$$

Let us introduce the characteristic parameters: density n_0 , temperature T_0 , distance $x_0 = 1/n_0 \pi \sigma^2$, velocity $v_0 = \sqrt{kT/m}$, time $\tau = x_0/v_0$, and transform in equations (14)-(17) to the dimensionless variables and the dimensionless function $f^* = f/n_0 v_0^{-3}$ (hereafter, "*" will be omitted). Let us consider two different values of the initial function:

$$\varphi_0(\xi) = \left(\frac{1}{2\pi T_1^{(0)}} \right)^{1/2} \left(\frac{1}{2\pi T_2^{(0)}} \right) \exp \left\{ - \left(\frac{\xi^2}{2T_1^{(0)}} + \frac{\rho^2}{2T_2^{(0)}} \right) \right\}, \quad (18) \quad \angle 56$$

where

$$\rho^2 = \eta^2 + \zeta^2; \quad \frac{T_1^{(0)} + 2T_2^{(0)}}{3} = 1, \quad \text{noting that } T_1^{(0)}/T_2^{(0)} = 2$$

and

$$\begin{aligned} \varphi'_0(\xi) = \frac{1}{2} \left(\frac{1}{2\pi T_0} \right)^{3/2} \left[\exp \left\{ - \frac{(\xi-1)^2 + \rho^2}{2T_0} \right\} + \right. \\ \left. + \exp \left\{ - \frac{(\xi+1)^2 + \rho^2}{2T_0} \right\} \right], \quad T_0 = 2/3. \end{aligned} \quad (19)$$

Condition (18) designates the nonequilibrium initial state of the gas, in which the energy is nonuniformly distributed over the successive degrees of freedom of the molecules. With time, smoothing of the temperatures must occur, $T_1 \rightarrow 1$ and $T_2 \rightarrow 1$, and the distribution function must approach the Maxwell equilibrium value.

Condition (19) represents the so-called "pseudojump" problem; attempts to solve it are given in reference [3], for example. This initial condition is convenient for the study of the evolution of the distribution function, since at $t=0$, it differs significantly from the Maxwell distribution function. Condition (19), like (18), corresponds to the Maxwell equilibrium distribution function, with $T_\infty = 1$ and $n_\infty = n_0 = 1$.

The deviation from equilibrium may be characterized by the quantity $T_1 - 1 = \Delta T_1$ or $T_2 - 1 = \Delta T_2$.

The results of three iterations for the initial value of (18) are shown in Figures 4, 5 and Table 1.

Curves 1, 2 and 3 in Figure 4 represent the results of one, two and three iterations, respectively, from the "zero" approximation

$$f_0 = \varphi_0(\vec{\xi}), \quad t = 0;$$

$$f_0 = f_0(\vec{\xi}) = \left(\frac{1}{2\pi}\right)^{3/2} \exp\left\{-\frac{\xi^2 + \rho^2}{2}\right\}, \quad t > 0.$$

The dashed curve gives the solution of the corresponding relaxation equation

$$\frac{\partial f}{\partial t} = -\nu_r (f - f_0), \quad (20) \quad \underline{57}$$

where $\nu_r = nT/\mu$.

The dependence of $\mu(T)$ for the considered model of solid elastic spheres is given in reference [4], for example.

In order to determine how close the results of three iterations are to the final solution of the problem, two iterations of the Boltzmann equation were used in solving the relaxation equation (20), used here as a "zero" approximation. The results of the comparison are given in Figure 5.

Curve 4 is obtained after two iterations for solving the relaxation equation. A small divergence of the curves is observed when t/τ is close to one, when the ΔT_1 value itself is small and the relaxation has basically terminated. This difference does not exceed 3% of the equilibrium temperature value.

Let us note that the characteristic time τ which we use here is not equal to the average time between collisions τ_0 , introduced in reference [4]:

$$\tau = \frac{4}{\sqrt{\pi}} \tau_0 \approx 2,26 \tau_0.$$

Table 1, which gives the density and temperature values, calculated by three iterations (n, T), and also by two iterations in solving the

relaxation equation (n', T'), is used in checking the calculations. In the problem considered, $n=1$ and $T=1$ for all values of $t \geq 0$, in view of the conservation laws. According to Table 1, the standard deviation does not exceed 0.5% for density and 1% for temperature.

Table 1

t/τ	n	n'	T	T'
0,10	0,997	0,998	0,989	0,989
0,25	0,998	0,997	0,988	0,936
0,40	1,006	0,992	1,002	0,992
0,55	1,007	1,016	0,995	1,008
0,70	1,017	1,002	1,008	0,999
0,85	1,009	1,014	1,005	1,008
1,00	1,000	1,015	0,996	1,005
1,15	1,003	1,013	0,998	1,007
1,30	1,010	1,007	0,998	1,001
1,45	0,998	1,009	0,991	1,003

Commas represent decimal points.

Figures 6 and 7, and Table 2, show corresponding results for the initial value of (19).

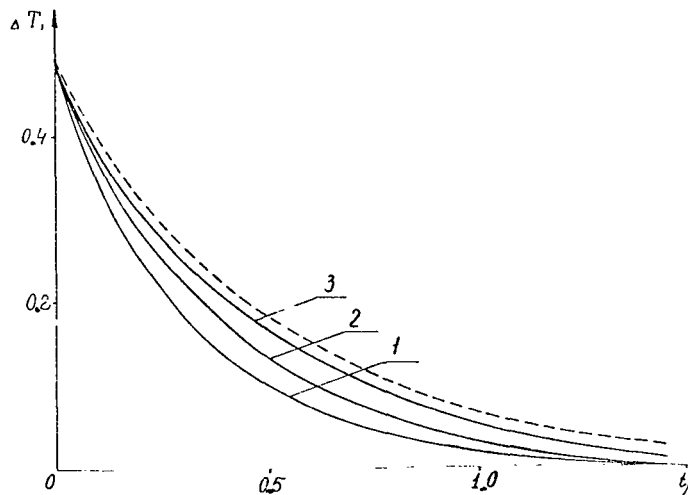


Figure 4. Solution of homogeneous relaxation problem (initial condition (18)): 1--first iteration; 2--second iteration; 3--third iteration; - - - - solution of the relaxation equation.

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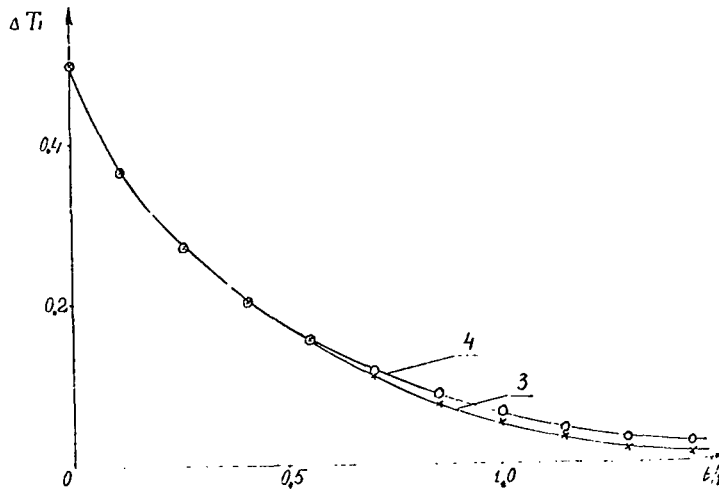


Figure 5: Comparison of iterations (initial condition (18)): 3--third iteration; 4--second iteration of the solution of the relaxation equation.

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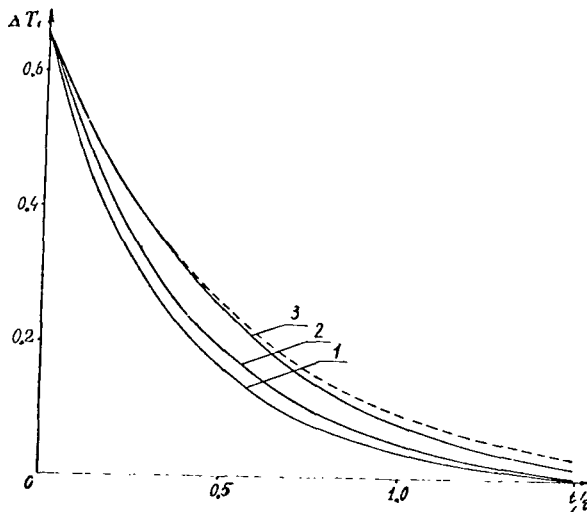


Figure 6: Solution of homogeneous relaxation problem (initial condition (19)): 1--first iteration; 2--second iteration; 3--third iteration; - - - - solution of relaxation equation.

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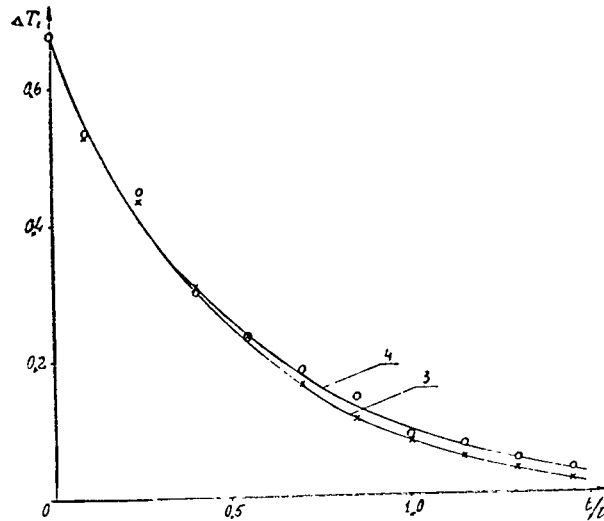


Figure 7. Comparison of iterations (initial condition (19)):
3--third iteration; 4--second iteration of the solution of the
relaxation equation.

In carrying out the calculations, the time steps were taken equal to 0.05τ . The hydrodynamic quantities were calculated by the trapezium method from 250 approximate distribution function values. In calculating $f^{(3)}(\vec{\xi}, t)$ when $t < \tau_0$, ten combinations were taken at each point $t_1 \leq t$; these combinations determine the values of the random vectors $(\vec{\xi}_1, \vec{\xi}, \vec{\xi}_1')$, which are the arguments of $f^{(2)}(\vec{\xi}, t_1)$, ($N_1=10$).

Corresponding $f^{(2)}(\vec{\xi}, t_1)$ values were calculated through $f^{(1)}(\vec{\xi}, t_2)$ from five combinations at each point $t_2 \leq t_1$ ($N_2=5$). The function $f^{(1)}(\vec{\xi}_1, t_2)$ is expressed analytically, using $f^{(0)}(\vec{\xi}, t_2)$.

Table 2

t/τ	n	n	T	T'
0,10	0,998	1,000	0,996	0,998
0,25	1,028	1,020	1,049	1,034
0,40	1,013	0,988	1,021	0,990
0,55	1,005	0,986	1,003	1,007
0,70	1,006	1,013	1,015	1,020
0,85	1,003	1,025	1,004	1,027
1,00	1,006	1,014	1,009	1,018
1,15	1,010	1,019	1,004	1,019
1,30	1,005	1,007	1,001	1,002
1,45	1,003	1,006	0,998	1,005

Commas represent decimal points.

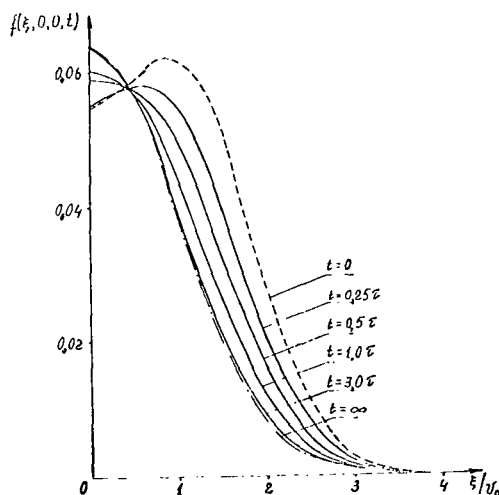
When $t > \tau_0$, the number of trials was taken to be $N_1 = 5$ and $N_2 = 3$. The complete calculation for three iterations required approximately five hours on a BESM-6 computer.

In calculating ΔT_1 and ΔT_2 in the second iteration approximation (curve 2 in Figures 4 and 6), the $f^{(2)}$ value was calculated using thirty trials at each $t_1 \leq t$ point. Complete computation took approximately twenty minutes.

Figure 8 represents evolution of the distribution function for the pseudojump problem (profile of distribution function $f^{(3)}(\vec{r}, 0, t)$). The dashed curve represents the distribution function values.

Figure 9, as a comparison, shows the distribution function profiles in the third iteration approximation $f^{(3)}$, in the first approximation $f^{(1)}$, and the solution of the relaxation equation f_r , for $t = 0.25 \tau$. Figure 9 explains the positions of the curves in Figure 6.

Similar results from distribution function calculations are shown in Table 3. The comparison of the $f^{(3)}$ and $f_r^{(2)}$ distribution functions obtained from the solution of the relaxation equation after two iterations, ^{/64} shows that the iteration approaches the solution of the Boltzmann equation with great accuracy.



^{/61}

Figure 8. Evolution of the distribution function in pseudojump problem.

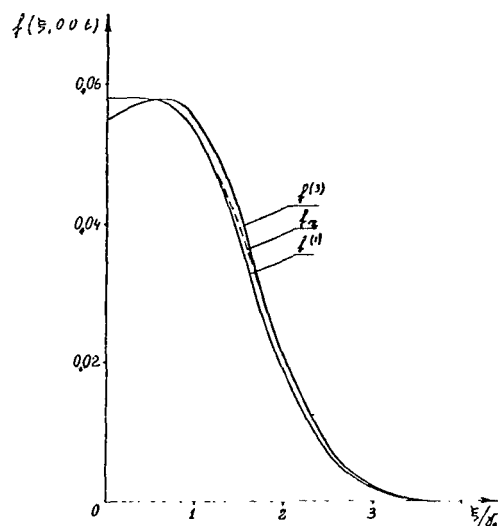


Figure 9. Comparison of distribution function profiles at the time $t = 0.25 \tau$: $f^{(1)}$ - first iteration; f_r - solution of relaxation equation; f^3 - third iteration.

Table 3

$t = 0,25$			$t = 0,5$		$t = 1$		$t = 1,5$		$t = 3$	
ξ	$f^{(3)}$	$f_r^{(2)}$	$f^{(3)}$	$f_r^{(2)}$	$f^{(3)}$	$f_r^{(2)}$	$f^{(3)}$	$f_r^{(2)}$	$f^{(3)}$	$f_r^{(2)}$
0	0,0558	0,0541	0,0593	0,0578	0,0638	0,0612	0,0622	0,0611	0,0635	0,0634
0,2	0,0565	0,0576	0,0576	0,0583	0,0601	0,0605	0,0611	0,0611	0,0626	0,0623
0,4	0,0577	0,0573	0,0580	0,0586	0,0574	0,0577	0,0597	0,0583	0,0590	0,0588
0,6	0,0567	0,0586	0,0553	0,0566	0,0561	0,0560	0,0541	0,0540	0,0534	0,0533
0,8	0,0579	0,0569	0,0535	0,0540	0,0489	0,0508	0,0483	0,0485	0,0465	0,0465
1,0	0,0536	0,0477	0,0486	0,0497	0,0442	0,0455	0,0409	0,0409	0,0388	0,0388
1,2	0,0502	0,0497	0,0451	0,0431	0,0370	0,0379	0,0331	0,0336	0,0310	0,0313
1,4	0,0440	0,0436	0,0365	0,0386	0,0299	0,0289	0,0263	0,0276	0,0240	0,0241
1,6	0,0362	0,0353	0,0298	0,0292	0,0225	0,0232	0,0196	0,0195	0,0178	0,0178
1,8	0,0276	0,0281	0,0220	0,0231	0,0169	0,0162	0,0139	0,0146	0,0127	0,0127
2,0	0,0200	0,0237	0,0173	0,0160	0,0117	0,0115	0,0098	0,0100	0,0086	0,0087
2,2	0,0139	0,0144	0,0110	0,0108	0,0077	0,0079	0,0032	0,0064	0,0057	0,0057
2,4	0,0096	0,0095	0,0072	0,0074	0,0048	0,0048	0,0039	0,0040	0,0036	0,0036
2,6	0,0063	0,0060	0,0042	0,0044	0,0027	0,0029	0,0024	0,0024	0,0022	0,0022
2,8	0,0035	0,0035	0,0024	0,0022	0,0016	0,0018	0,0013	0,0014	0,0013	0,0013
3,0	0,0018	0,0018	0,0014	0,0014	0,0009	0,0009	0,0008	0,0008	0,0007	0,0007
3,2	0,0011	0,0009	0,0007	0,0007	0,0005	0,0005	0,0004	0,0004	0,0004	0,0004
3,4	0,0005	0,0005	0,0003	0,0003	0,0002	0,0002	0,0002	0,0002	0,0002	0,0002
3,6	0,0002	0,0002	0,0002	0,0002	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001
3,8	0,0001	0,0001	0,0001	0,0001	0,00005	0,00005	0,00005	0,00005	0,00005	0,00005

Commas represent decimal points.

Table 4

t/τ	α_4	α_4'	α_4''	β_4	β_4'	β_4''	δ_4	δ_4'	δ_4''
0,10	5,484	5,481	5,684	2,569	2,572	2,461	1,073	1,075	1,067
0,25	4,760	4,756	5,024	2,609	2,879	2,784	1,061	1,054	1,044
0,40	4,295	4,251	4,521	3,195	3,205	3,040	1,067	1,051	1,028
0,55	3,855	3,873	4,137	3,275	3,457	3,231	1,027	1,034	1,013
0,70	3,539	3,583	3,844	3,592	3,547	3,377	1,017	1,021	1,003
0,85	3,336	3,385	3,620	3,701	3,675	3,488	1,009	1,025	0,996
1,00	3,193	3,280	3,450	3,734	3,726	3,572	0,994	1,012	0,989
1,15	3,073	3,203	3,320	3,790	3,791	3,637	0,993	1,007	0,985
1,30	3,019	3,134	3,220	3,811	3,788	3,681	0,984	0,997	0,981
1,45	2,978	3,076	3,145	3,814	3,829	3,724	0,977	0,993	0,979

Table 5

t/τ	γ_4	γ_4'	γ_4''	γ_6	γ_6'	γ_6''	γ_8	γ_8'	γ_8''
0,10	14,91	14,92	14,87	104,3	104,4	104,5	914,9	915,5	922,6
0,25	14,82	14,73	14,78	102,8	101,7	102,5	893,4	879,1	889,0
0,40	14,95	14,87	14,70	102,3	101,9	100,9	871,2	867,8	863,3
0,55	14,71	14,92	14,65	99,58	101,0	99,74	835,3	848,0	843,7
0,70	14,79	14,76	14,61	98,72	93,50	98,83	813,4	826,3	828,7
0,85	14,77	14,83	14,57	98,43	99,33	98,13	807,6	821,3	817,3
1,00	14,63	14,78	14,55	97,37	98,91	97,60	796,7	816,6	808,6
1,15	14,62	14,81	14,53	97,11	98,87	97,19	793,1	813,9	801,9
1,30	14,57	14,70	14,52	96,57	97,83	96,89	787,3	801,9	796,9
1,45	14,51	14,70	14,51	96,21	97,68	96,65	784,0	798,8	793,0

Table 6

t/τ	α_4	α_4'	α_4''	β_4	β_4'	β_4''	δ_4	δ_4'	δ_4''
0,10	5,499	5,509	5,625	2,189	2,668	2,077	1,076	1,074	1,072
0,25	4,940	4,962	4,977	2,890	2,730	2,498	1,097	1,097	1,048
0,40	4,328	4,314	4,483	3,063	2,908	2,816	1,072	1,034	1,030
0,55	3,957	4,024	4,106	3,227	3,257	3,060	1,0	1,043	1,016
0,70	3,648	3,708	3,819	3,548	3,513	3,246	1,032	1,048	1,005
0,85	3,383	3,502	3,599	3,605	3,641	3,388	1,015	1,047	0,997
1,00	3,283	3,418	3,432	3,695	3,710	3,496	1,013	1,032	0,990
1,15	3,129	3,245	3,304	3,784	3,807	3,579	0,996	1,020	0,986
1,30	3,061	3,153	3,206	3,796	3,740	3,642	0,990	1,000	0,982
1,45	3,005	3,079	3,132	3,825	3,810	3,690	0,985	0,995	0,979

Commas represent decimal points.

Table 7

/64

t/τ	γ_4	γ_4'	γ_4''	γ_6	γ_6'	γ_6''	γ_8	γ_8'	γ_8''
0,10	14,14	14,13	14,07	89,48	89,34	89,19	693,8	692,4	692,4
0,25	15,11	14,81	14,16	96,31	94,21	90,75	750,4	731,5	712,8
0,40	14,74	14,26	14,23	95,29	92,23	91,93	755,2	732,2	728,4
0,55	14,55	14,71	14,29	95,22	96,53	92,84	764,8	777,2	740,3
0,70	14,87	14,93	14,33	97,68	98,18	93,53	785,3	792,5	749,4
0,85	14,65	14,97	14,36	96,82	98,45	94,06	787,0	794,5	756,3
1,00	14,72	14,97	14,38	96,84	99,20	94,46	782,0	805,2	761,6
1,15	14,68	14,94	14,40	97,11	98,68	94,77	788,9	799,4	765,6
1,30	14,61	14,63	14,42	96,53	96,72	95,00	783,8	785,6	768,7
1,45	14,59	14,68	14,43	96,55	96,94	95,18	784,7	786,3	771,1

Commas represent decimal points.

In calculating the $f^{(3)}(\vec{\xi}, t)$ profile, 250 combinations determined the argument $f^{(2)}(\vec{\xi}, t_1)$, $t_1 \leq t$; ten combinations were used to determine the argument $f^{(1)}(\vec{\xi}, t_2)$, $t_2 \leq t_1$.

Tables 4 and 5 (initial condition (18)) and 6 and 7 (initial condition (19)) show the values of a number of higher moments of the distribution function:

$$\alpha_4 = \langle \xi^4 \rangle; \quad \beta_4 = \frac{1}{2} \langle \rho^4 \rangle; \quad \delta_4 = \frac{1}{2} \langle \xi^2 \rho^2 \rangle;$$

$$\gamma_4 = \langle (\xi^2 + \rho^2)^2 \rangle; \quad \gamma_6 = \langle (\xi^2 + \rho^2)^3 \rangle; \quad \gamma_8 = \langle (\xi^2 + \rho^2)^4 \rangle.$$

The prime designates the moment calculated from $f_r^{(2)}$, and the double prime designates moments calculated from the relaxation kinetic equation.

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THE STRUCTURE OF SHOCK WAVES IN A GAS
CONSISTING OF IDEALLY ELASTIC, RIGID SPHERICAL MOLECULES

F. G. Cheremisin

1. Principal Approaches to the Theoretical Study
of the Structure of the Shock Layer

Analysis of shock wave structure is one of the classical /65
problems of kinetic theory; a satisfactory solution has not yet been obtained.
Works dealing with this problem may be subdivided into three groups.

The first group contains those works in which a sufficiently rough
and, in essence, little justified approximation of the distribution function
and Boltzmann equation are replaced by a system of moment equations [1-3],
or Navier-Stokes equations are solved [4-5]. An important contribution to
evaluation of such attempts was made in [6, 7] in which it was
shown that there is no convergence in the Grad and Barnett expansion
with $M > 1.65$ and $M > 2.1$ respectively. When the Mach numbers are not very
close to 1, we know that the conditions for the applicability of the Navier-
Stokes equation (small changes of the hydrodynamic quantities over the
mean free path of the molecule) are not fulfilled; at best, one could
expect qualitatively reliable description of the transition layer.

The second group of works includes the solution of "model" kinetic
equations, the physical significance of which is close to that of the
Boltzmann equation [8]. For this equation it is possible to obtain an
exact numerical solution, which, one would expect, is qualitatively and
to a certain extent quantitatively close to the solution of the Boltzmann
equation.

The third group includes works in which, instead of the solution of
the kinetic equation, some statistical process which provides a relatively
correct model of the investigated phenomenon is used [9-11]. In this case,
as in the case of the Boltzmann equation, the solution is carried out at
the distribution function level, and consequently involves all of the diffi-
culties associated with the necessity of remembering functions with a /66

large number of variables. The volume of calculations is significantly decreased by abandoning the Boltzmann collision integral for a statistical model of individual molecular collisions. However, abandoning the kinetic equation has some drawbacks, in that the constructed random process does not adequately represent the true physical phenomenon. Perhaps these are the causes for the nonstatistical fluctuations on the profile of hydrodynamic quantities in the above works. Lack of memory space in electronic digital computers forces either subdivision of the phase space into quite large cells or limitation to a relatively small number of test particles, which leads to significant statistical noise, which makes isolation of the solution of the problem difficult.

In references [12, 13], the shock wave structure was investigated on the basis of one iteration of the Boltzmann equation, based on the gas dynamic discontinuous Rankine-Hugonio solution. The nonmonotonic behavior of the density, temperature and velocity curves is of some interest, but at the same time it indicates the necessity for further approximations.

2. The Presentation of the Problem; Choice of the Molecular Model

Rigorous treatment of the problem of the structure of shock waves necessitates solving the kinetic Boltzmann equation:

$$\xi \frac{\partial f}{\partial x} = J[f] \quad (1)$$

with boundary conditions

$$\left. \begin{aligned} f(\vec{\xi}; x = -\infty) &= f_0(\vec{\xi}; n_1, T_1, u_1); \\ f(\vec{\xi}; x = \infty) &= f_0(\vec{\xi}; n_2, T_2, u_2), \end{aligned} \right\} \quad (2)$$

where

$$f_0(\vec{\xi}; n, T, u) = \left(\frac{m}{2\pi T} \right)^{3/2} n \exp \left\{ - \frac{m(\vec{\xi} - \vec{u})^2}{2T} \right\}.$$

The parameters $n_1, T_1, u_1, n_2, T_2, u_2$ are associated with the Rankine-Hugonio conditions.

The solution found for $f(\vec{\xi}, x)$ must subsequently be used for calculation

of hydrodynamic quantities (density, temperature, velocity, momentum and energy transport), the behavior of which inside a jump is of fundamental physical interest.

Equation (1) with boundary conditions (2) shall be solved using an iteration "tree," as presented in the previous work of the author (this collection). Using this method, it was possible to carry out three iterations of the Boltzmann equation using a BESM-6 computer.

Ideally elastic spheres of constant diameter σ and with no internal degrees of freedom were taken as a molecular model of gas. The collision integral, given in expanded form in the above-mentioned work, can be transformed to the following form

$$J[f] = -v[f_1]f + N[f'f'_1], \quad (3)$$

where

$$v[f_1] = 2\pi\sigma^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_1 |q| d\xi_1 d\eta_1 d\zeta_1;$$

$$N[f'f'_1] = \pi^2 \sigma^2 \int_{-\infty}^{\infty} \int_0^1 \int_0^1 f'f'_1 |q| \sin(\pi\theta) d\theta d\varepsilon d\xi_1 d\eta_1 d\zeta_1.$$

The zero iteration is a solution of the model kinetic equation, which is obtained from (1) and (3) by substituting $v_r(n, T, \vec{u})$ for $v[f_1]$ and $v_r f_0(\vec{\xi}; n, T, \vec{u})$ for $N[f'f'_1]$.

In the rigid elastic sphere model the quantity v_r is equal to

$$v_r = \frac{nT}{\mu} = \frac{16}{5} n\sigma^2 \sqrt{\frac{\pi T}{m}}.$$

The purity of collisions is selected in such a manner that within the limits of the continuous medium the correct value of the viscosity coefficient is given, but a value of the thermal conductivity coefficient different from the true coefficient by 50% (since $Pr = 1$, and not $2/3$).

3. Numerical Calculation Method

The calculations were conducted for Mach number $M=2$. The boundary condition at $-\infty$ was transferred to a distance equal to -4.1λ from the initial

gas-dynamic discontinuity, while the condition at $+\infty$ was transferred to a distance of $+2\lambda$, where λ is the mean free path in the oncoming stream:

$$\lambda = 1/\sqrt{2} \pi \sigma^2 n_1.$$

Calculation tests revealed that further removal of the boundaries does not have any effect on the results. The integration region along the x-axis was subdivided into 431 equal segments δx , which determined the minimum magnitude of the step along the space coordinate.

By integrating equations (1) and (2) when $\xi > 0$ and when $\xi < 0$, we obtain

$$f(\xi > 0, x) = f_0(\vec{\xi}; n_1, T_1, u_1) \exp \left\{ -\frac{1}{\xi} \int_a^x v(\vec{\xi}, x_1) dx_1 \right\} + \frac{1}{\xi} \int_a^x N(\vec{\xi}, x_1) \exp \left\{ -\frac{1}{\xi} \int_{x_1}^x v(\vec{\xi}, x_2) dx_2 \right\} dx_1; \quad (4)$$

$$f(\xi < 0, x) = f_0(\vec{\xi}; n_2, T_2, u_2) \exp \left\{ -\frac{1}{|\xi|} \int_x^b v(\vec{\xi}, x_1) dx_1 \right\} + \frac{1}{\xi} \int_a^b N(\vec{\xi}, x_1) \exp \left\{ -\frac{1}{|\xi|} \int_x^{x_1} v(\vec{\xi}, x_2) dx_2 \right\} dx_1 \quad (5)$$

($a = -4, 1\lambda$; $b = 2\lambda$).

The integrals of the formula for model kinetic equations can obviously be obtained from (4) and (5).

One characteristic of expressions (4) and (5) is the factor $1/\xi$, which occurs during integration over x . If one assumes that the quantity $v(\vec{\xi}, x)$ is insignificantly dependent on ξ , then the "attenuation" of the exponents which enter into (4) and (5) is proportional to the quantity $1/\xi$. In order to achieve the necessary accuracy, the integral in which such attenuation occurs must contain a sufficient number of division points. As a result, the integration steps along the x-axis are selected to be dependent on ξ . In integrating the model equation it is assumed that

$$\Delta x = \delta x \left(1 + \frac{\xi}{k \delta x v_r} \right). \quad (6)$$

The quantity v_r is taken at that point at which the value of the distribution function is calculated. The factor k determines the number of exponent division points which are included in the attenuation integral, and aids in the best choice of calculation conditions.

In the integration of the Boltzmann equation, the quantity v_r in formula (6) is replaced by v_0 , the collision frequency, which is calculated from /69
the local Maxwell distribution function [14]

$$v_0(\xi; n, T, u) = \frac{n \sqrt{2T}}{\sqrt{\pi}} \left\{ e^{-\beta^2} + \frac{2\beta^2 + 1}{2\beta} \operatorname{erf}(\beta) \right\}, \quad (7)$$

where

$$\beta = \sqrt{\frac{(\xi - u)^2 + \eta^2 + \zeta^2}{2T}}.$$

The moments of the distribution function were calculated as functions of variables ξ , $\rho = \sqrt{\eta^2 + \zeta^2}$ by a regular method. Values of ξ were taken in the interval -3.5 to 5 thermal velocities and values of ρ were taken from zero to 4.3 thermal velocities. In solving the model equation and performing the first iteration of the Boltzmann equation for the calculation of moments at each point x , approximately 2500 values of the distribution function were taken. The moments in the second and third approximations were calculated by taking into account the convergence of the iteration, while the values of the distribution function in the previous iteration were used for increasing the accuracy of calculations. The differences in moments were calculated:

$$\Delta M_i' = M_i^{(2)} - M_i^{(1)} = \int \psi_i (f^{(2)} - f^{(1)}) d\xi;$$

$$\Delta M_i'' = M_i^{(3)} - M_i^{(2)} = \int \psi_i (f^{(3)} - f^{(2)}) dx.$$

In the second approximation, in order to achieve calculation accuracy on the order of one percent, 1000 values of the distribution function at each point x were sufficient. In the third iteration calculations, 250 values of $f^{(3)}$ ensured an accuracy of approximately 3%.

4. Solution of the Kinetic Relaxation Equation

Calculation of the shock wave structure on the basis of relaxation (model) kinetic equations may be considered an independent problem, the solution of which was obtained in the above-cited works for Sutherland's model of molecules. On the other hand, the problem of the solution of the relaxation equation may be viewed as a simplified variation of the program for the solution of the Boltzmann equation, in which the return to the subprograms for the collision integral is replaced by the calculation of the quantity v_r and $N_r = v_r f_0$.

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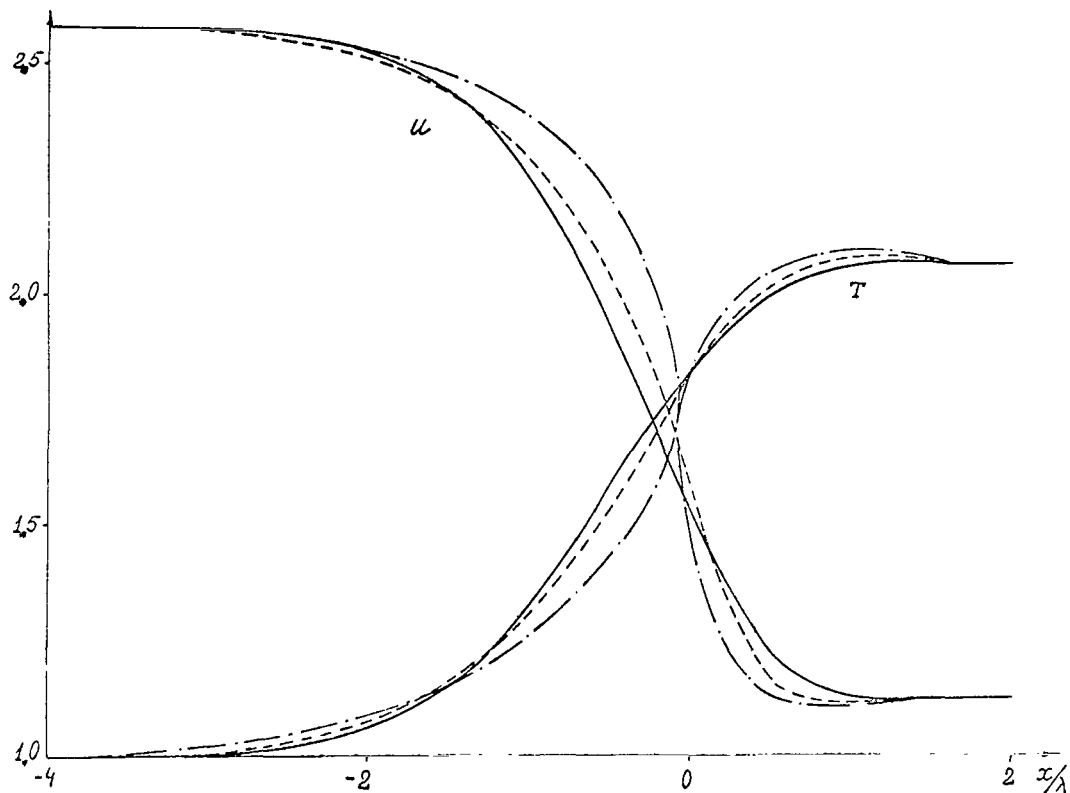
In solving the relaxation equation we also use the integrated iteration method, but, in contrast to the method used in [8], we did not use integral equations for density, temperature and the average velocity; rather, we made the calculations through computations of distribution functions in an appropriate iteration.

From the discontinuous values of $n^{(0)}$, $T^{(0)}$ and $u^{(0)}$, we calculated the distribution functions in the first iterative approximation; from the function thus obtained we calculated the values of $n^{(1)}$, $T^{(1)}$ and $u^{(1)}$, which were placed in the memory for each of the 431 subdivision points along the x-axis; the process then was repeated until the iterations converged.

This differed from method [8] principally in that we used a gas dynamic discontinuity, rather than the smooth solutions of the Navier-Stokes equation, as the zero approximation.

The iteration based on gas dynamic discontinuity is simpler, since it does not require preliminary solution of the Navier-Stokes equation; however, in this case an undesirable phenomenon occurs: there are "humps" on the $n(x)$, $T(x)$, and $u(x)$ curves to the right of the initial jump (Figure 1) (thus, the "humps" noted in reference [12] result from the initial discontinuity). In subsequent iterations these "humps" dissipate and shift towards $+\infty$; they thus distort the boundary conditions to the right of the jump. We applied the method of improving convergence by artificial "truncation of the "humps" as soon as they appear. Figure 1 shows that with each new iteration, less and less correction is required. By the end of the sixth or seventh iteration, the magnitude of the "humps"

is equal to the accuracy of calculations (0.5%), and the iterations themselves converge with the same order of accuracy.



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Figure 1. Solution of the kinetic relaxation equation;
- - - - first iteration; - . - third iteration; — seventh iteration.

For future reference, it is important to note that the principal approach to the solution is achieved in the first three iterations, even if the discontinuity profile is used as the "zero" approximation.

Some qualitative explanation for this may be given by considering formulae (4) and (5). In both formulas, the first term to the right dominates the second term at distances from the boundary of order λ ; in this region the first iteration considerably reconstructs the initial distribution

function. However, the solution of the problem shows that the jump thickness is $\sim 3\lambda$ and three iterations are required in order to cover the whole transition region.

5. Solution of the Boltzmann Equation

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The n , T , and u profiles calculated from the kinetic model equation were recorded on magnetic tape and served as the basis for subsequent iterations of the Boltzmann equation. The zero iteration was taken to be the local Maxwell distribution function $f_0(\vec{\xi}; n, T, u)$, with parameter values which are solutions of the model equation. Such a choice makes it possible to reduce the calculations in the first iteration, since the integrals $v_0[f_0]$ and $N_0[f_0'f_{01}']$ are analytically expressed through the vector $\vec{\xi}$ and the parameters n , T , and u , the quantity v_0 is given by formula (7) and N_0 is determined from the equilibrium condition

$$N_0 = v_0 f_0.$$

The choice of the local Maxwell distribution function as the zero iteration allows the use of the decreased dispersion method, based on the identical transformation of the collision integral

$$\begin{aligned} v^{(1)}[f^{(1)}] &\equiv v^{(1)}[f^{(1)} - f^{(0)}] + v_0; \\ N^{(1)}[f^{(1)'}f_1^{(1)'}] &\equiv N^{(1)}[f^{(1)'}f_1^{(1)'} - f^{(0)'}f_1^{(0)'}] + N_0. \end{aligned}$$

Analogous calculations of $v^{(2)}$ and $N^{(2)}$ are made.

Each value of the distribution function in the third iteration $f^{(3)}$ was calculated from an average of 200 $f^{(2)}$ values; the calculation of a single $f^{(2)}$ value required approximately 200 $f^{(1)}$ values, while $f^{(1)}$ was calculated from approximately 15 $f^{(0)}$ values. When carrying out two iterations the $f^{(2)}$ function was calculated at each $(\vec{\xi}, x)$ point from 600 $f^{(1)}$ values. The integration results are represented in Figures 2-5. The density and temperature values refer to the values in the oncoming stream, and the selected velocity scale is $v_0 = T_1/m$.

Figure 2 shows the agreement of the values of hydrodynamic parameters calculated in the first, second, and third iterations of the Boltzmann equation.

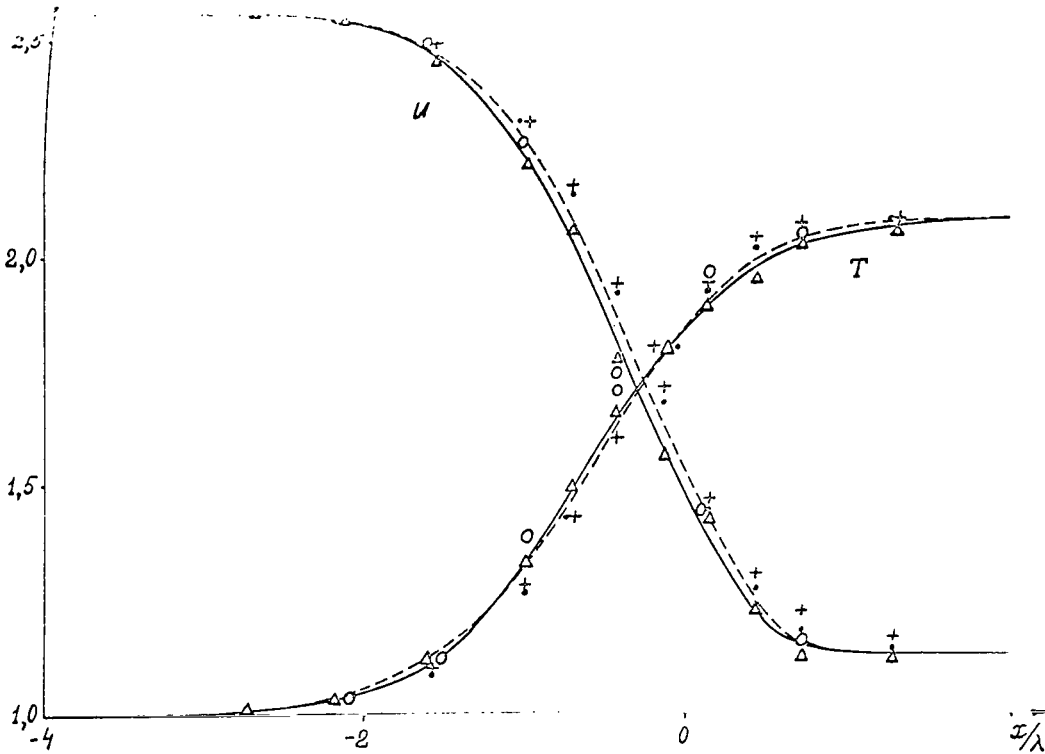


Figure 2: Solution of the Boltzmann equation; first iteration; +++++ second iteration; $\Delta\Delta\Delta\Delta$ third iteration; oooo third iteration on another initial profile; - - - solution of the relaxation equation.

In order to evaluate the obtained approximation of a precise numerical solution of the problem, the equation for the conservation of mass flow in a plane shock wave is used:

$$j = n(x)u(x) = n_1 u_1. \quad (8)$$

Since relationship (8) is not used in carrying out the successive iterations of the Boltzmann equation, the deviation of the calculated mass flow from its true value permits judgment regarding the convergence of the iterations and the degree of the achieved approximation to solution of the problem.

In the second iteration the average deviation $\langle \Delta j^{(2)} \rangle = 0.12$, which is approximately 4.5% of the j value with a mean relative error of 1% in calculating $j^{(2)}$.

In the third iteration the average deviation $\langle \Delta j^{(3)} \rangle = -0.05$, which is approximately 2% of the j value and approximately equal to the mean relative error in calculating $j^{(3)}$.

One would expect that the same approximate accuracy of convergence to the true solution of the Boltzmann equation could be achieved. Integration at a number of points on the x -axis was performed (circles in Figure 2) as an additional check on the convergence of the iterations, starting with a second "zero" iteration.

The local Maxwell function was used as the second "zero" iteration; values of $n(x)$, $u(x)$, and $T(x)$ were calculated from the first iteration of the Boltzmann equation.

Figure 2 shows that within the limits of statistical computation error the values found for $u(x)$ and $T(x)$ coincide with the earlier calculated values.

Figure 2 also shows $u(x)$ and $T(x)$ profiles calculated from the kinetic relaxation equation. The closeness of the density, temperature and velocity values obtained from the relaxation and Boltzmann equations are apparently attributable to the fact that at relatively small M numbers, the principal role in forming shock wave structure is played by the viscosity processes; thermal conductivity is a secondary process, whose role is reduced to some redistribution of the heat released in the shock layer [15].

The kinetic relaxation equation which we used with a frequency chosen with "viscosity" taken into account, gives the correct expression for the viscosity coefficient and thus describes viscous energy dissipation well.

Figure 3 shows the change in the thermal flux in the shock layer. It can be seen that the relaxation equation gives a significantly different $Q(x)$ value.

$$\text{Here } Q(x) = \frac{1}{2} \int (\xi - u) [(\xi - u)^2 + \eta^2 + \zeta^2] f(\vec{\xi}, x) d\vec{\xi}.$$

Figure 4 shows the changes in entropy $S = 1/n \int f \ln f d\vec{\xi}$ in the shock wave. Let us note the difference between the accepted Boltzmann determination of entropy and the thermodynamic entropy $S_v = c_v \ln(p/\rho^\gamma)$, which is used in

the description of the method based on the Navier-Stokes equation; it assumes conditions to be close to local thermodynamic equilibrium.

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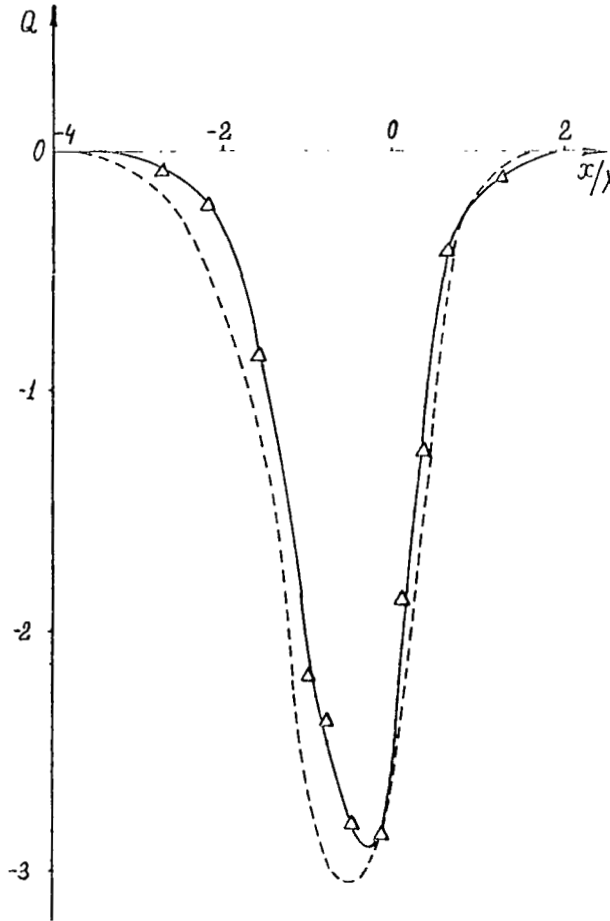


Figure 3. Thermal flux in a shock wave; Δ - third iteration; - - - relaxation equation.

Figure 5 shows that the local thermodynamic equilibrium conditions in a shock wave of average intensity are not fulfilled: the gas possesses two significantly different temperatures, of translational degrees of freedom: longitudinal temperature T_{11} and transverse temperature T_{22} . By definition:

$$T_{11} = \frac{1}{n} \int (\xi - u)^2 f d\vec{\xi};$$

$$T_{22} = \frac{1}{2n} \int (\eta^2 + \zeta^2) f d\vec{\xi}.$$

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The $u(x)$ and $T(x)$ curves are used in computing shock wave thickness; it is defined by the formula [16]:

$$d_{\Gamma} = \frac{\Gamma_2 - \Gamma_1}{(d\Gamma/dx)_{\max}}.$$

The obtained values are $d_T \sim 2\lambda$ and $d_u \sim 2\lambda$; these agree with Tamm's estimate reported in reference [1].

Figure 6 gives the profile of the distribution function $f(\xi, 0, 0, x)$, calculated for three different points inside the shock layer.

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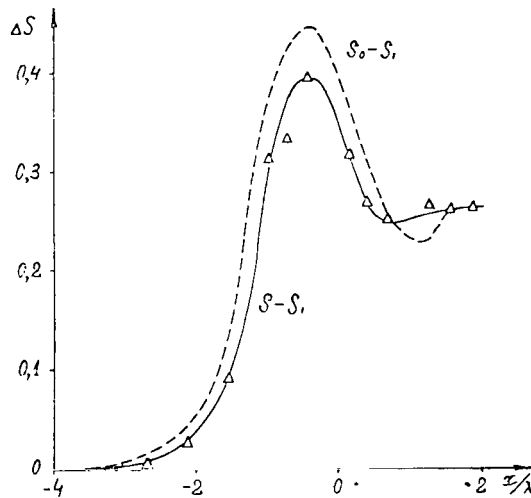


Figure 4. Change of entropy in the shock wave; _____ entropy according to Boltzmann; - - - thermodynamic entropy.

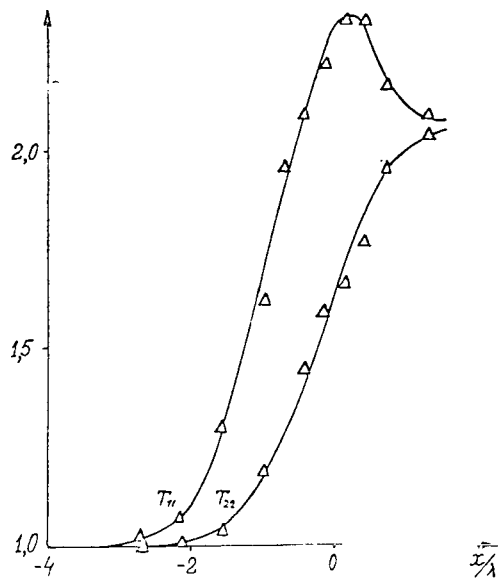


Figure 5. Longitudinal temperature T_{11} and transverse temperature T_{22} in the shock wave.

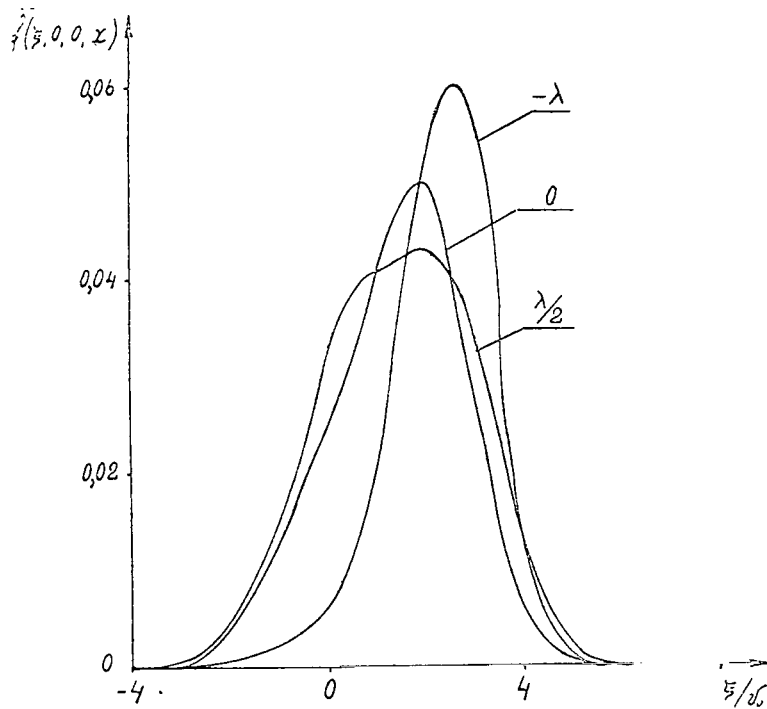


Figure 6. Distribution function profile at three points inside the shock layer.

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THE SOLUTION OF THE RELAXATION PROBLEM FOR THE BOLTZMANN EQUATION BY THE INTEGRAL ITERATION METHOD

Ye. F. Limar

One of the simplest problems involving the Boltzmann equation is the problem of relaxation of some initial distribution function which depends only on velocities, to Maxwell's distribution function. Earlier, this problem was solved by Wachman and Hamel [1] by the discrete ordinate technique [1]. The results obtained in this work have shown that the proposed variation of the method is not effective in a "nonlinear" case, since in this case the density decreases significantly with time. Other methods used for the same problem were those of F. G. Cheremisin [2] and Ye. M. Shakhov [3] in the work published in this collection. /79

Let us write the Boltzmann equation for the relaxation problem in which the distribution function $f(t, u, v)$ is time dependent and is also dependent on two other variables u and v (the velocities of rigid spherical molecules) and in a cylindrical coordinate system:

$$f = f_0 \exp\left(-\int_0^t L dt\right) + \int_0^t G \exp\left(-\int_\tau^t L d\xi\right) d\tau, \quad (1)$$

here

$$L(f) = 2\pi \int_{-\infty}^{+\infty} \int_0^\infty \int_0^{2\pi} f(u_1, v_1) v_1 \sqrt{(u-u_1)^2 + v^2 + v_1^2 - 2vv_1 \cos(\psi - \psi_1)} \times \\ \times d\psi_1 dv_1 du_1 -$$

is the collision frequency;

$$G(f) = \int_{-\infty}^{+\infty} \int_0^\infty \int_0^{2\pi} \int_0^\pi f(u', v') f(u_1', v_1') |w| v_1 \sin \theta d\theta d\varphi d\psi_1 dv_1 du_1 -$$

is the integral of return collision.

The relative velocity of the colliding particles in the cylindrical coordinate system has the form /80

$$w = (u - u_1) \cos \theta + \sin \theta (v \cos(\psi - \varphi) - v_1 \cos(\psi_1 - \varphi)),$$

and the velocity of molecules after the collision is represented as follows:

$$\begin{aligned}v' &= \sqrt{v^2 + w \sin \theta (w \sin \theta - 2v \cos(\psi - \varphi))}; \\v'_1 &= \sqrt{v_1^2 + w \sin \theta (w \sin \theta + 2v_1 \cos(\psi_1 - \varphi))}; \\u' &= u - w \cos \theta; \quad u'_1 = u_1 + w \cos \theta.\end{aligned}$$

Equation (1) is written in dimensionless form; in doing this, the following relationships are utilized:

$$\begin{aligned}\vec{v} &= \vec{v}^* \sqrt{m/2\pi kT}; \quad f(\vec{v}) = f^*/n \left(\frac{m}{2\pi kT} \right)^{3/2}; \\t &= t^* \left(\frac{m}{2\pi kT} \right)^{-1/2} \frac{\sigma^2 n}{2}.\end{aligned}$$

In these expressions, the quantities with asterisks are dimensional. Equation (1) was solved by the iteration method; as the zero iteration solution of the model Krook's equation was used, which in dimensionless form may be written as follows:

$$f(t, u, v) = (f_0 - f_\infty) \exp[-4.525t] + f_\infty,$$

here

$$f_\infty = f(t = \infty, u, v) = \exp[-\pi(u^2 + v^2)], \quad (2)$$

and as the initial distribution function, a function of the following form is selected

$$f_0 = \alpha_1 \exp(-\beta_1[(u - U_1)^2 + v^2]) + \alpha_2 \exp(-\beta_2[(u + U_2)^2 + v^2]), \quad (3)$$

where due to the earlier assigned form of the distribution function (2) when $t = \infty$, six parameters in the expression (3) were related by three equations, indicating time independence of density n , and temperature T , and the average velocity equaling to zero.

The iteration process was carried out as follows. The velocity space u, v was subdivided into squares, the distribution function in each square being approximated by the second-order surface from the values of the distribution function at nine points. The set of all of these points forms a network of u, v values at the nodes of which the distribution function can be found from formula (1). The time integrals were calculated by the trapezoid method, while the L and G integrals were found by the Monte Carlo

method. It should be noted that a significant part of the machine time is

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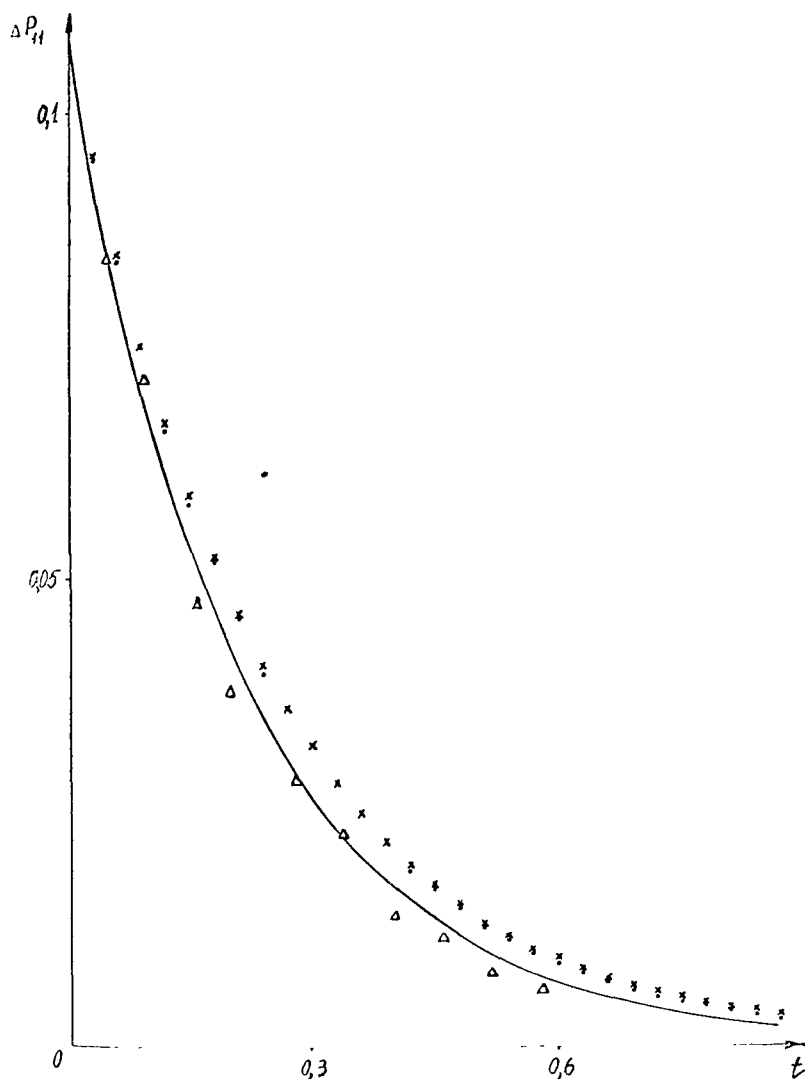


Figure 1. Relaxation of the additional stress ΔP_{11} :

— relaxation of Krook equation;
 first iteration; xxx fourth iteration;
 ΔΔΔ F. G. Cheremisin's [2] solution.

used in calculating the velocities of molecules after the collision, therefore, in this work the L and G integrals were calculated for all t values simultaneously. This permits a significant reduction in calculation time. In calculating the L and G integrals certain methods for the reduction of the distortion were used [4], which also reduced the computer time. At the end of

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each iteration, coefficients of the approximating expression and the moments of the distribution functions were determined. The computation time for one iteration on a BESM-6 computer for various combinations varied from 3 to 30 minutes; the latter corresponded to the computation of integrals based on a sampling of 1,000 combinations.

Certain calculation results are shown in Figures 1 and 2, where changes of the moments are shown:

$$\Delta P_{11} = 2\pi \iint (f(u,v) - f_{\infty}(u,v)) u^2 v \omega du dv;$$

$$S = -2\pi \iint (f(u,v) - f_{\infty}(u,v)) uv (u^2 + v^2) du dv$$

and

$$\Delta n = 2\pi \iint (f(u,v) - f_{\infty}(u,v)) v du dv;$$

$$\Delta T = 2\pi \iint (f(u,v) - f_{\infty}(u,v)) v (u^2 + v^2) du dv$$

as a function of time for symmetrical initial functions with parameters

$$\alpha_1 = \alpha_2 = 0,92; \quad \beta_1 = \beta_2 = 4,71; \quad U_1 = U_2 = 1/\sqrt{2\pi}.$$

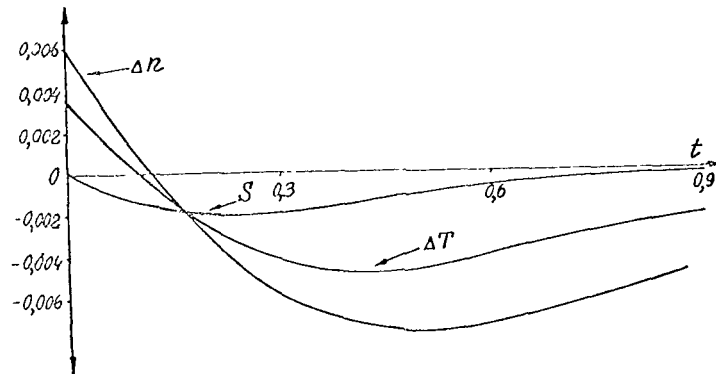


Figure 2. Time dependence of the additional moments ΔT , Δn and S .

The curves for deviations of density, temperature and heat flux from their equilibrium values give some idea concerning the accuracy of the calculation results, since in this case they must be constant and equal to zero.

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For the above-mentioned initial function, which is characterized by a small deviation from equilibrium at the initial moments, calculations have shown rapid convergence of the integral iteration method. In attempting calculation from the initial function, which exhibits a large and asymmetrical deviation from equilibrium [3], it was found that the calculations accuracy is reduced and as a result, after a certain number of iterations the results begin to diverge. The reduction in accuracy is associated with the fact that in this variation of calculations Maxwell's distribution function was subtracted in order to reduce dispersion in calculation of the L and G integrals.

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Ye. M. Shakhov

Introduction

The basis for the kinetic theory of gases is the Boltzmann equation. /84
The difficulties involved in its solution are well known. These difficulties result, first, from the large number of arguments in the distribution function (in the general case equal to seven); second, they are due to the complex structure of the collision integral.

The most promising idea for solving these problems is derived from the theory of rarefied gases, wherein principal attention is given to several first moments of the distribution function, i.e. certain average characteristics. This means that the behavior of the distribution function in this region of changing molecular velocities, which does not change the value of the pertinent moments (i.e., especially in the region of very large and very small characteristic molecular velocities), is not significant. This idea is used in different ways in various methods for solving problems in the theory of rarefied gases.

In the moments method, the distribution function is not calculated at all, but is assigned more or less arbitrarily with an accuracy to several macroscopic parameters, which are subsequently determined from the system of moment equations. In direct numerical solutions of the kinetic equation, the above considerations are used first of all in choosing the limits for the region of change in the characteristic molecular velocity (the bounded region is considered to be "infinite," if in the rejected part the distribution function is so small that it does not significantly change the values of the pertinent first moments; the higher moments are generally not taken into account), and secondly, directly in the calculation process /85
(the calculation of many quantities, defining the distribution function, is carried out with low accuracy).

In an earlier work [1] the author proposed a method for approximating the Boltzmann equation (more accurately, for the Boltzmann collision

integral), based on requirements of equality of several first moment relationships from the precise and approximate collision operator. The purpose of the approximation is to replace the structurally complex collision integral of the Boltzmann equation with a significantly simpler one which preserves the principal characteristics of the Boltzmann equation only to the extent dictated by the necessity of sufficiently accurate calculation of the pertinent distribution function moments.

The idea of replacing the collision integral is not new. After the relaxation model of the collision integral was proposed [2], kinetic model equations became the subject of many investigations (for example, see [3, 4, 5]). The most interesting of these works, devoted to generalization of the Krook equation, was carried out in the investigations of Holway [6].

The general method ordinarily used in constructing kinetic models is as follows. On the basis of physical considerations, reverse collision and collision frequency integrals are selected as functions of molecular velocities and a system of certain macroscopic parameters. The collision integral of the selected form conforms to the conservation equations, which leads to a decrease in the number of independent macroparameters; they may even (as in the case of Krook's model) be expressed in part through the distribution function moment. If the conditions for satisfying the conservation equation do not lead to expression of the necessary number of macroparameters through the distribution function moment, one can assume their dependence on the moments (as in Holway's model [6]). The remaining undefined macroparameters are determined from the condition of the coincidence of stresses and thermal fluxes in the limiting transition to a continuous medium, using the Enskog-Chapman method.

Aside from this general method, which is ordinarily used in constructing the kinetic equations, the Gross and Jackson method can be used for constructing the linearized Boltzmann equation models [7]; this is based on the use of the eigenfunctions of the linearized collision operator for the Maxwell molecular model. In contrast to the already-described

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Krook and Holway method, which leads finally to one model, this method gives a regular procedure for constructing a sequence of kinetic model equations. In spite of the specificity of the Gross and Jackson method, Sirovich [8] made an attempt to apply this method to the nonlinear Boltzmann equation by expanding the distribution function which enters the collision integral using Hermitian polynomials. As already noted, the Krook-Holway method in its ordinary form does not permit the construction of a sequence of model equations. However, the possibility of generalizing and constructing consecutive approximate kinetic equations is inherent in the method itself, if one views it from the standpoint of moment equations.

In fact, requiring that the conservation equations be satisfied is equivalent to the combination of conditions of the equality of moments from the collision integral of the zero, first, and one moment of the second order to the corresponding moments of the Boltzmann collision integral. The requirement of converting to a continuous medium can also be expressed by means of moment equations, not by the Enskog-Chapman method. For example, for the relaxation model in the Krook form it is sufficient to use second-order moment equations and to impose the requirement that all moments from the collision integral to the second order inclusive coincide with the corresponding moments of the Boltzmann collision integral with a constant collision frequency (independent of the molecular velocities). By increasing the number of conditions imposed on the moments of the collision operator and selecting it in a definite form, one can obtain consecutive approximate kinetic equations with an approximate (in the moments sense) collision operator, which was in fact proposed in [1].

Let us note that the Gross and Jackson method is essentially also based on the use of the moment relationships for the collision integral, since eigenvalues of the linearized collision operator are in fact its moments.

This work is devoted to further development of a method for approximating the Boltzmann equation. A case of pseudo-Maxwellian molecules is considered in detail. A method of approximating the

collision frequency is discussed. A method for approximating moments of the Boltzmann collision integral is proposed. The approximation of the collision frequency and collision integral moments enables one to reduce each kinetic equation approximating the Boltzmann equation to a form which differs very little in complexity from Krook's model equation, since the return collisions integral and the collision frequency are expressed through the distribution function moments. For the approximating equations the same numerical method is applicable as for Krook's equation; the most promising is the discrete velocities method [5].

Since the principal results of the work refer to the approximation of the collision integral which determines the relaxation process, two problems on relaxation in homogeneous unbounded space are solved as examples.

1. General Approximation Scheme
for the Boltzmann Equation

To determine the state of rarefied gas, we shall examine the gas in the absence of any external forces. The principal kinetic equation of the theory of gases, the Boltzmann equation, is written in the form

$$\left. \begin{aligned} \frac{\partial f}{\partial t} + \xi_i \frac{\partial f}{\partial x_i} &= J^+(f) - \nu(f)f; \\ J^+(f) &= \int \int f' f'_1 g d\sigma d\vec{\xi}_1; \quad \nu(f) = \int \int_1 g \sigma d\vec{\xi}_1; \\ d\sigma &= b db d\epsilon; \quad g = |\vec{\xi} - \vec{\xi}_1|, \end{aligned} \right\} \quad (1)$$

where $f(t, x_i, \xi_i)$ is the distribution function; ξ_i is the molecular velocity vector; g is the modulus of the relative velocity of colliding molecules; b and ϵ are collision parameters; σ is a collision cross section; summation over the recurring indices is proposed. We shall define the distribution function moments in the ordinary way:

$$\begin{aligned} \rho &= mn = m \int f d\vec{\xi}; \\ \bar{u}_i &= m \int \xi_i f d\vec{\xi}; \\ P_{ij} &= m \int c_i c_j f d\vec{\xi}, \quad c_i = \xi_i - u_i; \\ S_{ijk} &= m \int c_i c_j c_k f d\vec{\xi}; \end{aligned}$$

$$Q_{ijkl} = m \int c_i c_j c_k c_l f d\vec{\xi};$$

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$$S_i = S_{ijj}; \quad p_{ij} = P_{ij} - p \delta_{ij}; \quad p = \frac{1}{3} P_{ii},$$

where m is molecular mass and δ_{ij} is the Kronecker delta.

If the function f satisfies the Boltzmann equation, then, as is well known, its moments satisfy the infinite system of moment equations, obtained by multiplying (1) by $1, \xi_i, \xi_i^2, \xi_i \xi_j, \xi_i \xi_j \xi_k$, etc., and subsequent integration over the entire velocity space. Here it is assumed that at high velocities ξ_i , f decreases quite rapidly, so that all the integrals are real. However, this does not mean that the system of moment equations (even an infinite one) is equivalent to the Boltzmann equation. The reverse argument, that if the system of distribution function moments satisfies the moment equations, the distribution function itself satisfies the Boltzmann equation, has no substance, since we do not know how to convert a system of moment equations to the Boltzmann equation. In order to make this possible, additional assumptions regarding the expression of the distribution function through the moments and regarding the smoothness of these moments and their convergence must be made.

The structure of moment equations is well known [5, 9], and we shall not give them here.

In addition to the precise kinetic equation, let us consider the approximate equation

$$\frac{\partial F}{\partial t} + \xi_i \frac{\partial F}{\partial x_i} = Q(F, \xi_i, a(t, x_i)), \quad (2)$$

where Q is an approximate collision operator which depends on the distribution function F , molecular velocities and some set of macroscopic functions, designated by a single letter $a(t, x_i)$. The form of the operator Q is thus still random.

We shall call equation (2) an equation which approximates the Boltzmann equation in the moment sense, if a certain number of first-moment equations of the approximating and precise kinetic equations coincide. Since the differential parts of equations (1) and (2) coincide, the differential part of the moment equations must also coincide. Consequently, a necessary and sufficient condition for the coincidence of the moment equations is an equality of the corresponding moments of the approximate and precise

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collision operators, i.e.

$$\int Q \psi d\vec{\xi} = \int J(F) \psi d\vec{\xi}, \quad (3)$$

$$\psi = 1, \xi_i, \xi_i \xi_j, \xi_i \xi_j \xi_k, \dots$$

More rigorously, equation (2) will be called an approximating equation of the n^{th} approximation for the Boltzmann equation if conditions (3) are fulfilled for all ψ , which includes power-law monomials with respect to velocity components of the n^{th} order. If in the n^{th} order approximation not all power-law monomials of the n^{th} order are used, but only part of them, the approximation will be called an incomplete n^{th} order approximation.

Equations (3) for the assigned form of the operator Q as a function of F , ξ_i and $a(t, x_i)$, serve as the definition of the set of macroscopic quantities $a(t, x_i)$ at each point in physical space at each moment of time; the number of unknowns must be the same as the number of equations.

Conditions (3) have a simple physical meaning. In fact, for a random distribution function $F(t, x_i, \xi_i)$, the quantity $F d\vec{\xi}$ is the number of molecules $\vec{\xi}$ (i.e., at velocities within $\vec{\xi}$ to $\vec{\xi} + d\vec{\xi}$ limits) at the point x_i of the physical space at time t . The quantity $J(F) d\vec{\xi}$ is the rate in change of the number of molecules $\vec{\xi}$ as a result of collisions, and the quantity $\xi_i \xi_j J(F) d\vec{\xi}$, for example, is the rate of change in the momentum flux component due to changes in the number of molecules $\vec{\xi}$ resulting from collisions, where the integral of $\xi_i \xi_j J(F) d\vec{\xi}$ is the rate of change in the same momentum component due to the collisions of all molecules.

Thus, conditions (3) require that the operator Q have the conservation of properties of an exact collision operator with respect to the quantities determined for all colliding molecules: the rate of change in the number of particles, momentum, energy, momentum flux, etc.

Equation (2) with an approximate collision operator satisfying conditions (3), even if the choice of Q is not made specifically as a function of F , ξ_i and $a(t, x_i)$, leads to some interesting conclusions. Specifically, moment equations obtained from (2) with conditions (3) give accurate solutions for any finite number of the first moments of the distribution

function of spatially uniform flows of a Maxwellian gas [10, 11]. This conclusion follows directly from the coincidence of the moment equations and the precise equations with a sufficient number of indefinite functions $a(t, x_i)$ and given initial conditions for the sought moments. It also follows from the coincidence of movement equations for motions of Maxwellian gas close to equilibrium that precise Navier-Stokes equations may be obtained in a conventional manner [9, 5]. /90

2. Form of an Approximate Collision Operator

Let us now choose the form of the Q operator. In order for equation (2) to approximate the fundamental kinetic equation (1) as well as possible, it is necessary to select Q in that form which is closest to the form of the Boltzmann collision integral. By analogy with the J integral, we shall take Q in the form

$$Q = Q^+ - NF, \quad (4)$$

where Q^+ and N are the approximate operator of the return collisions and the approximate collisions frequency, respectively.

The separation of Q into operators of direct and return collisions, i.e., representation in the form of (4), is highly significant, since the direct collision integral NF describes correctly (in the qualitative sense) the scattering of a random beam of molecules with any fixed velocity in a medium of other gas molecules.

The Q^+ and N operators will be considered functions of the thermal velocities of molecules c_i and some set of macroscopic parameters $a(t, x_i)$ and $b(t, x_i)$:

$$Q^+ = Q^+(c_i, a(t, x_i));$$

$$N = N(c_i, b(t, x_i)).$$

In order to determine the set $a(t, x_i)$ and the set $b(t, x_i)$, one can use moment relationships of type (3), but separately for the return collision integral and the direct collision integral:

$$\int \psi Q^+(\vec{\xi}, a(t, x_i)) d\vec{\xi} = \int \psi J^+(F) d\vec{\xi}; \quad (5)$$

$$\int \psi N(\vec{\xi}, b(t, x_i)) F d\vec{\xi} = \int \psi v(F) F d\vec{\xi}, \quad (6)$$

$$\psi = 1, \xi_i, \xi_i \xi_j, \xi_i \xi_j \xi_k, \dots$$

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Moment relationships (3) are automatically satisfied in this case. Let us represent Q^+ in the same form that J^+ has in the Maxwellian distribution function, i.e., in the form of the product of the collision frequency N and some F^+ characterizing the velocity distribution of molecules after collisions,

$$Q^+ = N(c_i, b(t, x_i)) F^+(c_i, a(t, x_i)).$$

With Q^+ of the selected form, the complete collision integral Q is represented in the form

$$Q = N(F^+ - F). \quad (7)$$

Representation in form (7) is expedient in that it satisfies most efficiently the conditions of local equilibrium flow or complete statistical equilibrium. For convenience in subsequent references, we shall rewrite relationship (3) with the use of (7)

$$\int N(F^+ - F) \psi d\vec{\xi} = \int J(F) \psi d\vec{\xi} = \int (\psi' - \psi) F F_1 g d\sigma d\vec{\xi} d\vec{\xi}_1, \quad (8)$$

$$\psi = 1, \xi_i, \xi_i \xi_j, \xi_i \xi_j \xi_k, \dots$$

Assuming the collision frequency to be known (the question of the approximation of N will be considered in Section 4), we shall turn to the choice of the form of the F^+ function. The only necessary condition for the F^+ function is that when the process approaches equilibrium (complete or local) this function must converge to the Maxwell function. All other characteristics of F^+ are fairly arbitrary.

From the physical standpoint it is tempting to apply the most probable distribution principle for the choice of F^+ , as was proposed in [6] for the collision frequency, nondependent on velocities. Generalization to the random frequency case is not difficult, since it plays no role in choice of the F^+ form.

We shall introduce the moments of function F^+ as the system of macro-parameters $a(t, x_i)$; these, in a certain sense, can be interpreted as density, momentum, temperature, etc., of the colliding particles. By assuming a certain number of moments F^+ to be known and using the principle of the most probable distribution, we obtain an exponential expression for F^+ , containing in the exponent a certain polynomial for the thermal velocities of the molecules, with coefficients expressed through the F^+ moments. The F^+ moments themselves are expressed as the moments of the collision integral using integral relationships (3) or (5).

Specifically, if consideration is limited to the first five moments, /92 corresponding to invariant collisions, then F^+ can be obtained in the form of the Maxwell functions with density, velocity and temperature of the colliding molecules, i.e., a generalized Krook's model with the frequency of collisions dependent on the velocity of molecules [3] is obtained. If all second-order F^+ moments are taken into account, an ellipsoidal distribution [6] is obtained.

When using the maximum probability principle for the choice of F^+ , it must be remembered that the integrals may diverge [12, 5]. However, this difficulty can easily be avoided by appropriate choice of the F^+ moments which are used as additional conditions for determining the most probable distribution.

A more significant difficulty, arising from the use of the F^+ function in the considered form is that equations (3) and (5) for determining the system of macroscopic parameters are complex transcendental equations which must be solved at each point t, x_i . However, one can assume that F^+ is close enough to the local Maxwell distribution function $F^{(0)}$ that it can be represented in a simpler form [1]:

$$\left. \begin{aligned} F^+ &= F^{(0)} (a^{(0)} + a_i^{(1)} c_i + a_{ij}^{(2)} c_i c_j + a_{ijk}^{(3)} c_i c_j c_k + \dots); \\ F^{(0)} &= \frac{n}{(2\pi RT)^{3/2}} e^{-c^2/2RT}. \end{aligned} \right\} \quad (9)$$

When F^+ is in form (9) and the stipulated collision frequency is N , moment relationships (8) comprise a system of linear algebraic equations

with respect to the expansion coefficients (9).

If necessary, the representation of F^+ (9) may be improved by replacing $F^{(0)}$ by a Maxwell function corresponding to the average parameters of the molecules participating in collisions, i.e., by the most probable function for the stipulated density, average velocity and the temperature of the colliding molecules. Parameters of this most probable function are determined by the conservation equations. The number of parameters which are contained in (9) must be decreased. Instead of (9) we shall have an expression

$$F^+ = F_c^{(0)} (1 + a_{ij}^{(2)} c_i^+ c_j^+ + a_{ijk}^{(3)} c_i^+ c_j^+ c_k^+ + \dots); \quad (10)$$

$$a_{ii}^{(2)} = 0; \quad c_i^+ = \xi_i - u_i^+,$$

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Here $F_c^{(0)}$ is the Maxwell function with parameters n^+ , u_i^+ and T^+ , corresponding to the colliding molecules. These parameters and the coefficients $a_{ij}^{(2)}$, $a_{ijk}^{(3)}$, etc., expressed through the F^+ moments are obtained as solutions of a system of equations obtained from (8) when F^+ is in form (10) and ψ , equal to 1, ξ_i , ξ_i^2 , $(1-\delta_{ij})\xi_i\xi_j$, $\xi_i\xi_j\xi_k$, etc.

Henceforth we will consider expression (9) to be the principal approximating formula for F , in which, apparently, one can convert from power monomials to Hermitian polynomials.

Thus, for the return collisions integral we obtain the principal approximating formula in the form

$$Q^+ = NF^+ = NF^{(0)} [a^{(0)} + a_i^{(1)} c_i + a_{ij}^{(2)} c_i c_j + \dots], \quad (11)$$

where the expansion coefficients (11) are defined by the moment relationships (8) or relationships (5). In other words, it is proposed that the return collisions integral be approximated by the finite sum of the corresponding Fourier series.

Let us note that the application of the Enskog-Chapman method to the Boltzmann equation gives the following expression for the return collision integral

$$J^+ = v^{(0)} f^{(0)} \left[1 + \frac{p_{ij}}{2pRT} \left(1 - \frac{p}{\mu v^{(0)}} \right) c_i c_j + \frac{S_i c_i}{5pRT} \left(1 - \frac{2}{3} \frac{p}{\mu v^{(0)}} \right) \right] \quad (12)$$

where $f^{(0)}$ is the local Maxwell distribution function; $\nu^{(0)}$ is the collision frequency determined from the local Maxwell functions, and μ is the gas viscosity coefficient.

In order for the Fourier series (11) for the return collisions integral to converge in the least squares sense, existence of the following integral is sufficient

$$\int \frac{[J^+(F)]^2}{NF^{(0)}} d\vec{\xi}.$$

However, the average convergence in the entire unbounded velocity space, associated with the condition of sufficiently rapid attenuation at infinity, has no significance if we are interested in the behavior of third and lower-order distribution function moments.

From this standpoint it is important to have uniform convergence of $J^+(F)$ and the distribution function in that part of the unbounded region in which the behavior of F produces the most significant contribution to the value of the first moments which are of interest to us. The behavior of the distribution function for very high velocities, on which higher moments are dependent, has no significance and in numerical calculations is not taken into account. This situation, as well as the fact that for any F function the reverse collisions integral $J^+(F)$ is a continuous velocity function, real at each point of the physical space x_i at random time t , indicates uniform and sufficiently rapid convergence of the solution with respect to the distribution function moments.

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In concluding this section let us note the following: formulation (11) for the return collisions integral is analogous in form to that proposed by Grad [9] for representation of the distribution function in the form of a series (or a finite sum) in Hermitian polynomials, multiplied by the local Maxwell distribution function. The principal difference between $J^+(F)$, in the case of stipulated F functions and the distributing function itself is that $J^+(F)$ is a local velocity function, determined at each fixed point in the physical space, in this function playing the role of a parameter, whereas the distribution function itself characterizes the state of the gas as a whole in the whole phase space region. For $J^+(F)$, therefore, representation in the form of a function with separable variables of type (11) is

admissible from the physical point of view. For the distribution function, on the other hand, such a representation is unnatural, since it stipulates a certain local gas state with the accuracy of the expansion coefficients; i.e., it assigns parameters of state, which are then determined from some differential or integral equations, averaged over the velocity. The principal characteristic of the rarefied gas, associated with the free motion of molecules over a significant distance (exceeding in order of magnitude the dimensions of the elementary cells of the physical space, which from the macroscopic standpoint may be considered infinitesimal), is that the distribution function has a significant component in which the variables t, x_i, ξ_i enter as combinations $x_i - \xi_i t$, while the representation of F in the form of an expansion with separable variables is lost. From this standpoint it is apparent that the distribution functions in the form

$$F = F^{(0)} (1 + \alpha_{ij} c_i c_j + \alpha_{ijk} c_i c_j c_k + \dots)$$

can describe only the hydrodynamic motion of gas.

3. Approximation of Boltzmann Equation for Pseudo-Maxwellian Gas

In the two previous sections a general approximation scheme was described on the basis of moment relationships for the collision integral, and the form of an approximate return collisions operator was selected assuming the collision frequency to be known. Approximation of the collision frequency will be considered in detail in the next section. Here we shall consider the problem of approximating the principal kinetic equation for pseudo-Maxwellian gases, i.e., for gases consisting of spherical molecules with collision cross sections inversely proportional to the relative velocity of the colliding molecules. In this case the collision frequency is independent of the relative velocity of the colliding molecules, which is the simplest approximation for the collision frequency. Moreover, when all moments of the collision integral are expressed through the distribution function moments, the questions of satisfying the equilibrium condition and the transformation to Euler and Navier-Stokes equations can be solved in an elementary fashion.

Let us assume, by analogy with the Krook relaxation equations, that where

$$N = \int F_1 g \sigma d\vec{\xi} = \frac{1}{\tau} = \frac{p}{\mu},$$

μ is the gas viscosity coefficient and F^+ , as before, is described in formula (9).

Consider immediately the second approximation, i.e., preserve the power monomials in (9) up to and including the second power.

In equations (8), instead of system

$$\psi = 1, \xi_i, \xi_i \xi_j$$

we can write

$$\psi = 1, c_i, c_i c_j.$$

Considering that for pseudo-Maxwellian molecules

$$I_{ij} = m \int c_i c_j J d\vec{\xi} = -\frac{p}{\mu} p_{ij}, \quad (13)$$

we obtain

$$a^{(0)} = a_i^{(1)} = a_{ij}^{(2)} = 0.$$

Thus, we obtain a Krook's model equation as the second approximating equation:

$$\frac{\partial F}{\partial t} + \xi_i \frac{\partial F}{\partial x_i} = \frac{1}{\tau} (F^{(0)} - F).$$

For the third approximation, we shall limit ourselves to representation of F^+ as a form of convolute Hermitian polynomials. Represent

$$F^+ = F^{(0)} \left\{ a^{(0)} + a_i^{(1)} c_i + a_{ij}^{(2)} \left(\frac{c_i c_j}{RT} - \delta_{ij} \right) + a_i^{(3)} c_i \left(\frac{c^2}{2RT} - \frac{5}{2} \right) \right\}.$$

To determine a set of coefficients $a(t, x_i)$ from (8), we can also make use of the corresponding orthogonal polynomials

$$\psi = 1, c_i, \frac{c_i c_j}{RT} - \delta_{ij}, c_i \left(\frac{c^2}{2RT} - \frac{5}{2} \right).$$

If, in addition to (13), we take into account the equation

$$I_{ijj} = m \int c_i c^2 J d\vec{\xi} = -Pr \frac{p}{\mu} S_i, \quad Pr = \frac{2}{3},$$

we obtain

$$a^{(0)} = a_i^{(1)} = a_{ij}^{(2)} = 0; \quad a_i^{(3)} = (1 - \text{Pr}) \frac{4}{5} \frac{S_i}{\rho (2RT)^2},$$

here Pr is the Prandtl number.

Thus, as the approximating equation of the incomplete third approximation, we obtain a generalized Krook equation

$$\left. \begin{aligned} \frac{\partial F}{\partial t} + \xi_i \frac{\partial F}{\partial x_i} &= \frac{1}{\tau} (F^+ - F); \\ F^+ &= F^{(0)} \left[1 + (1 - \text{Pr}) \frac{S_i c_i}{5 p R T} \left(\frac{c^2}{2RT} - \frac{5}{2} \right) \right]. \end{aligned} \right\} \quad (14)$$

Let us note that F^+ according to (14) coincides exactly with F^+ as defined in the first approximation using the Enskog-Chapman method (see (12)).

From the moment equations obtained by multiplying (14) by $1, \xi_i, \xi_i^2, \xi_i \xi_j, \xi_i \xi_j^2$ and subsequent integration over the whole velocity space, we obtain a Navier-Stokes equation with correct values of the viscosity and thermal conductivity coefficients when $\tau \rightarrow 0$. /97

Equation (14) may also be called the eight-moment approximation kinetic equation, since F^+ is determined by eight moments. It is consequently possible to construct a closed system of integral equations with respect to the moments n, u_i, T , and S_i . From this standpoint the Krook equation is a five moment kinetic equation. In contrast to the thirteen moment Grad approximation, obtained by formal closure of the moment equations, the system closure in this case takes place through the kinetic equation, so that the behavior of the distribution function at some point t, x_i is determined by the distribution of moments in the whole region, not by the values of these moments at the considered point.

This approximation process can be continued. Here, due to the orthogonality of the Hermitian polynomials with the weighting function $F^{(0)}$, system (3) is solved in an explicit form and the coefficients $a^{(0)}, a_i^{(1)}, \dots$ are expressed through the distribution function moments. Thus, sets of equations which approximate the Boltzmann equation are obtained. These equations can be viewed as model equations for random molecules.

The principal difference between this approach and Holway's method

of constructing the model equation [6] is, as already noted in the introduction, the use of condition (3) for the moments of the approximate collision integral; this enables the development of a regular procedure for constructing approximate kinetic equations from a single viewpoint. The form of the F^+ function may also be selected on the basis of the most probable distribution principle.

Let us also note that the generalized kinetic Krook model, which insures the correct Prandtl number in transition to a continuous medium, can be obtained in another form by using moment relationships up to the second order and selecting the collision frequency by an appropriate method, as was done in [6].

Let us now consider the equilibrium solutions of approximate equations in a homogeneous unbounded state. Turning to moment equations (8) when F^+ is in form (9), we will obtain zeros on the left, since at equilibrium the following must hold:

$$F = F^+.$$

Consequently, for equation (14), for example, we obtain

$$S_i = 0,$$

i.e., in the case of a Maxwellian equilibrium distribution, it is the only one possible.

Let us now turn to the Boltzmann H-theorem, by means of which the uniqueness of the Maxwell distribution is established as the equilibrium solution of the Boltzmann equation. Unfortunately, rigorous proof of the H-theorem with F^+ in the form (9) is not possible, since F^+ and consequently F , can be negative. However, one can expect that for most cases the expansion coefficients (9) will be sufficiently small, and F will be negative only in the region of very high velocities, where F itself is small.

Consider the case of small deviations from equilibrium in a homogeneous space and limit analysis to equation (14), the simplest of the approximate kinetic equations which insure the correct Prandtl number.

Multiplying the left and right sides of equation (14) for the case of homogeneous space, after an obvious transformation of the right-hand side we obtain,

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$$\frac{\partial H}{\partial t} = -\frac{1}{\tau} \int (F-F^+) \ln \frac{F}{F^+} d\vec{\xi} + \frac{1}{\tau} \int (F^+ - F) \ln F^+ d\vec{\xi}, H = \int F \ln F d\vec{\xi}.$$

Taking advantage of the smallness of S_i , we linearize $\ln F^+$ and utilize moment relationship (8), thus obtaining, when $Pr = 2/3$,

$$\frac{\partial H}{\partial t} = -\frac{1}{\tau} \int (F-F^+) \ln \frac{F}{F^+} d\vec{\xi} - \frac{8}{45} \frac{S_{ii}^2}{\rho(2RT)^3}. \quad (15)$$

According to (15), the Boltzmann H-function decreases with sufficiently small deviations from equilibrium. However, as we have already seen, the question of the uniqueness of the Maxwell distribution at equilibrium gives a unique solution regardless of whether or not it is possible to prove the H-theorem for the corresponding approximate equation.

4. Approximation of Collision Frequencies

The question of whether or not it is possible to consider molecules pseudo-Maxwellian and, consequently, to assume the collision frequency to be independent of molecular velocities, depends on the conditions of the problem and the gas properties. Conditions do exist under which it is not possible to dismiss in advance the dependence of collision frequency on the velocity of molecules.

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In this section we shall consider possible ways of approximating collision frequencies.

In reference [1] it was proposed to utilize the collision frequency determined from the local Maxwell distribution function, i.e., instead of the frequency

$$N = \int F_1 |\vec{\xi} - \vec{\xi}_1| \sigma d\vec{\xi} = \int F_1 |\vec{c} - \vec{c}_1| \sigma d\vec{\xi}_1$$

using the frequency

$$N^{(0)} = \int F_1^{(0)} |\vec{c} - \vec{c}_1| \sigma d\vec{\xi}_1. \quad (16)$$

For most problems this formula apparently gives sufficiently good approximations for N , since in general it correctly describes the dependence of collision frequency on velocity. In particular, for large c ,

$$N \sim N^{(0)} \sim n \sigma c.$$

Other approximate collision frequency formulas, determined by the specific conditions of the problem, are also possible.

In principle, moment relationships (6) for the return collisions integral make possible a more exact formulation of any initial collision frequency approximations. In fact, by assigning deviation from $N^{(0)}$, for instance, defined by formula (17), in the form of a series of some functions of c_i for determining the coefficients in this series, from (6) we obtain a system of linear equations.

Keeping in mind that deviations of N from $N^{(0)}$ must be maximum near the boundaries or initial conditions, the frequency determined from the distribution function in the form

$$\bar{F} = F_0 e^{-\int_{t_0}^t N^{(0)} d\tau} + F^{(0)} [b^{(0)} + b_i^{(1)} c_i + \dots] \left(1 - e^{-\int_{t_0}^t N^{(0)} d\tau} \right),$$

will give a good approximation of the collision frequency; F_0 and t_0 correspond to the initial boundary conditions of the problem. The $b(t, x_i)$ coefficients are defined by relationship (6). However, multiple integrals over a complex region of integration arise.

A simpler way of approximating the collision frequency (if N is not sufficiently well approximated by $N^{(0)}$) apparently lies in using approximation 100 formulas for the relative velocity g of the colliding molecules. Let us, for instance, use the expansion for low and for high velocities. For simplicity, consider the case when the collision cross section σ is independent of g .

For small c values we have the formula:

$$N = N_0 + \left(\frac{\partial N}{\partial c_i} \right)_0 c_i + \frac{1}{2} \left(\frac{\partial^2 N}{\partial c_i \partial c_j} \right)_0 c_i c_j. \quad (17)$$

The subscript "0" indicates that the quantity was taken when $c = 0$. The values of the derivatives in (17) are expressed by the formulas:

$$\left(\frac{\partial N}{\partial c_i} \right)_0 = -\sigma \int \frac{c_i}{c} F d\vec{\xi};$$

$$\begin{aligned}\left(\frac{\partial^2 N}{\partial c_i^2}\right)_0 &= \sigma \int \frac{1}{c} \left(1 - \frac{c_i^2}{c^2}\right) F d\vec{\xi}; \\ \left(\frac{\partial^2 N}{\partial c_i \partial c_j}\right)_0 &= \sigma \int \frac{c_i c_j}{c^2} F d\vec{\xi}, \quad i \neq j.\end{aligned}$$

For velocities c with sufficiently large modulus, one can utilize an asymptotic expansion of N . Let us write g in the form

$$g = \sqrt{c^2 + c_1^2 - 2s} = c \sqrt{1 + \frac{c_1^2}{c^2} - 2 \frac{s}{c^2}}, \quad s = c_i c_{i1}.$$

For $c \gg c_1$, the following holds:

$$g = c \left(1 + \frac{c_1^2}{2c^2} - \frac{s}{c^2} - \frac{1}{2} \frac{s^2}{c^4} + \dots \right). \quad (18)$$

with second order accuracy for the very small residuals. By substituting this expansion into the collision frequency expression, we obtain the following asymptotic representation of N :

$$N \approx \frac{\sigma}{m} \left(\rho c + \frac{p}{c} - \frac{p_{ij} c_i c_j}{2c^3} + \dots \right). \quad (19)$$

At equilibrium, when $p_{ij} = 0$, we obtain an asymptotic expression which coincides with the asymptotic expression for the local equilibrium collision frequency for spherical molecules,

$$N^{(0)} = \frac{n}{\sqrt{\pi}} \sqrt{2RT} \left\{ e^{-v^2} + \left(2v + \frac{1}{v} \right) \int_0^v e^{-x^2} dx \right\}, \quad v = \frac{c}{\sqrt{2RT}}.$$

Formulas (17)-(19) give expressions for the collision frequency through the distribution function moments.

5. Approximation of the Collision Integral Moments

The collision integral moments are the most complex expressions of all those which have been considered. In the general case, they are

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expressed by eight-dimensional integrals (integration over the collision parameters and double integration over velocity space). It is true that integration over the collision parameters can be done analytically, which reduces the integrals to six-dimensional form. For specificity, let us limit ourselves to the case of elastic spheres of cross section σ and cite formulas for the collision integral moments $c_i c_j$ and $c_i c^2$:

$$\left. \begin{aligned} l_{ij} &= m \int (c'_i c'_j - c_i c_j) d\sigma FF_1 g d\vec{\xi} d\vec{\xi}_1 = \frac{m\sigma}{2} \int \left[(c_{i1} c_{j1} - c_i c_j) - \frac{1}{2} (c_{i1} - c_i)(c_{j1} - c_j) \right] g FF_1 d\vec{\xi} d\vec{\xi}_1, \quad i \neq j; \\ l_{ij} &= m \sigma \int \left[-c_i^2 + c_i c_{j1} + \frac{1}{4} (c_i - c_{i1})^2 + \frac{1}{12} g^2 \right] g FF_1 d\vec{\xi} d\vec{\xi}_1, \quad i \neq j; \\ l_{ijj} &= m \int (c'_i c'^2 - c_i c^2) d\sigma FF_1 g d\vec{\xi} d\vec{\xi}_1 = m \sigma \int \left[-c_i c^2 + \frac{1}{2} (c_i + c_{i1}) s + \frac{1}{3} (u + u_1) g^2 \right] g FF_1 d\vec{\xi} d\vec{\xi}_1, \\ g &= |\vec{\xi} - \vec{\xi}_1|, \quad s = c_i c_{i1}. \end{aligned} \right\} \quad (20)$$

Integration over the collision parameters for random molecules which are the force centers is done in an elementary (but quite exhausting) way, this being particularly true for the moments of the fourth and higher orders. A rational way of calculating these integrals was proposed by Maxwell and described in detail in the works of Boltzmann [13] and Ikenberry and Truesdell [14].

Integration of the collision integral moments, typical examples of which are integrals (20), is conducted without separation of variables, due to the presence of the relative velocity. In the case of Maxwellian or pseudo-Maxwellian molecules,

$$\sigma \sim 1/g; \quad d\sigma \sim 1/g$$

the separation of variables is performed, and integrals are reduced to the distribution function moments. Specifically, integrals (20) acquire the form:

$$l_{ij} = -\frac{p}{\mu} p_{ij}; \quad l_{ijj} = -\frac{2}{3} \frac{p}{\mu} S_i. \quad (21)$$

The formulas for the derivatives of third-order moments may be found in [9, 5], while the fourth- and fifth-order moments can be found in [15, 14]. Thus, the model of Maxwellian molecules significantly simplifies the situation.

We do not actually know how real molecules behave, or how valid the model for molecular interaction is. Conclusions regarding the collision cross sections are generally drawn on the basis of transfer coefficient data. The simplification of the collision moment integrals can formally be done by setting $g = \text{constant}$ (when $\sigma = \text{constant}$), not $\sigma \sim g^{-1}$, and selecting the constant in such a way that equation (21) is satisfied. Such a viewpoint is not without foundation. In fact, a distribution function which differs little from the Maxwell distribution function in the first (and a very good) approximation would have the same formulas (21), independently of the molecular model selected.

It is thus possible to attempt approximation of the moments of the collision integral by approximating the relative velocity g . Let us assume approximately

$$\int (\psi' - \psi) g F F_1 d\sigma d\vec{\xi} d\vec{\xi}_1 = g_0 \int (\psi' - \psi) F F_1 d\sigma d\vec{\xi} d\vec{\xi}_1,$$

where g_0 is some unknown value of the relative velocity modulus. The values of the integrals, for small distribution function deviations from the Maxwellian make possible an accurate selection of g_0 from the fulfillment of the condition (21). Here the g_0 quantity is found to be the same for both integrals (21):

$$g_0 = 2 \frac{p}{\sigma n \mu}$$

Since in the general case the g_0 value selected in such a manner is approximate, one can use an expansion in the g_0 region for g . Keeping in mind that the FF_1 function rapidly decreases with an increase in the arguments (and consequently g), one can hope to obtain a good asymptotic evaluation of the integral by limiting ourselves to a linear approximation for relative velocity. Assuming that

$$g = \sqrt{g^2} = g_0 + \frac{1}{2g_0} (g^2 - g_0^2) + \dots \quad (22)$$

and substituting the obtained expansion into the formulas for the collision

integral moments, we obtain an expression for the latter through the distribution function moments. Specifically, in the linear approximation the I_{ij} , I_{ijj} moments are represented in the form

$$\left. \begin{aligned} I_{ij} &= -\frac{p}{\mu} p_{ij} + \left\{ \frac{1}{2} \frac{p}{\mu} p_{ij} + \frac{\sigma}{2mg_0} \left[-p Q_{ijkk} - \right. \right. \\ &\quad \left. \left. - 5pp_{ij} - p_{ik}p_{jk} \right] \right\}, \quad i \neq j; \\ I_{ij} &= -\frac{p}{\mu} p_{ij} + \left\{ \frac{1}{2} \frac{p}{\mu} p_{ij} + \frac{\sigma}{2mg_0} \left[-p \left(Q_{ijkk} - \frac{1}{3} Q_{iikk} \right) - \right. \right. \\ &\quad \left. \left. - \frac{7}{2} pp_{ij} - \frac{2}{3} p_{ij}^2 + \frac{1}{3} p_{kk}^2 - \frac{1}{3} p_{ik}p_{jk} \right] \right\}, \quad i = j; \\ I_{ijj} &= -\frac{2}{3} \frac{p}{\mu} S_i + \left\{ \frac{1}{3} \frac{p}{\mu} S_i + \frac{\sigma}{2mg_0} \left[-\frac{p}{3} \int c_i c^4 F d\vec{\xi} - \right. \right. \\ &\quad \left. \left. - \frac{5}{3} p_{ij} S_j + \frac{2}{3} S_{ijk} p_{jk} \right] \right\}. \end{aligned} \right\} \quad (23)$$

In the random model of molecules, when the collision cross section σ may depend on relative velocity, this requires utilization not of expansion (22), but of the corresponding expansion of the σg product in the $\sigma_0 g_0$ region, where

$$\sigma_0 g_0 \approx \text{const} = 2 \frac{p}{\mu n}.$$

Here the model of molecular interaction determines the dependence of viscosity on temperature.

6. The Problem of Isotropic Relaxation in a Homogeneous Space

The proposed method for approximating the Boltzmann equation does not apply to the differential part of the equation, only to the collision integral. Since in the collision integral the point coordinates in physical space play the role of parameters, the possibility and effectiveness of the proposed approximation method can be significantly clarified in the example of gas relaxation in a homogeneous space. /104

In this and in subsequent sections, we present the results of the numerical solution of two problems of gas relaxation in a homogeneous space. In the first problem the distribution of molecules by velocities is assumed to be isotropic (the distribution function depends on the velocity

modulus), while in the second case it is axially symmetric. The solution of the first problem is compared with the exact numerical solution of V. A. Rykov [16], while the solution of the second problem is compared with the solution of F. G. Cheremisin [17]. The collision frequency is assumed to be an equilibrium frequency, i.e., it is calculated from the Maxwell distribution function. The model for the molecules is elastic spheres of diameter d .

Thus, the problem is solved with the initial data for the equation

$$\frac{\partial F}{\partial t} = N^{(0)}(F^+ - F). \quad (24)$$

Here and in the subsequent section all quantities are assumed to be dimensionless; time is reduced to the mean time between collisions t^* , molecular velocity to c^* , distribution function to F^* , where

$$t^* = (4nd^2\sqrt{\pi RT})^{-1}; \quad c^* = \sqrt{2RT}; \quad F^* = \frac{4\sqrt{2}}{9} \frac{n}{(2\pi RT)^{3/2}}.$$

The frequency $N^{(0)}$ for solid spheres has the form [18]:

$$N^{(0)} = \frac{\sqrt{2}}{4} \left\{ e^{-c^2} + \left(2c + \frac{1}{c} \right) \int_0^c e^{-x^2} dx \right\} \quad (25)$$

Let us first consider the problem of isotropic relaxation. In this case, in view of the collision integral simplifications, it is relatively easy to obtain an accurate numerical solution [16].

In view of the distribution function isotropicity, all odd moments are equal to zero. The F^+ function is selected in the form

$$F^+ = F^{(0)} (1 + \alpha + \beta c^2 + \gamma c^4); \quad F^{(0)} = \frac{9}{4\sqrt{2}} e^{-c^2} \quad (26)$$

i.e., one utilizes the fourth approximation. For determining the unknown coefficients α , β , γ , which are time dependent, according to (8) we have a system of linear algebraic equations:

$$\int N^{(0)}(F^+ - F) \psi d\vec{c} = \frac{2}{9\pi\sigma} \int (\psi' - \psi) F F_1 g d\sigma d\vec{c} d\vec{c}_1, \quad \psi = 1, c^2, c^4. \quad (27)$$

The conservation laws require that the right-hand sides of the first two /105
equations be equal to zero. In the third equation the integral is reduced to a two-dimensional integral:

$$\begin{aligned} \frac{2}{9\pi\sigma} \int (c'^4 - c^4) F F_1 g d\sigma d\vec{c} d\vec{c}_1 = \\ \frac{4}{9} \int_0^\infty \int_0^\infty F(c) F(c_1) c c_1 \times \left\{ -\frac{1}{12} \frac{(c+c_1)^7 - |c-c_1|^7}{7} + \frac{c^2+c_1^2}{6} \frac{(c+c_1)^5 - |c-c_1|^5}{5} + \right. \\ \left. + \left[\frac{(c^2+c_1^2)^2}{4} - c_1^4 \right] \frac{(c+c_1)^3 - |c-c_1|^3}{3} \right\} d c d c_1. \end{aligned}$$

The coefficients of the linear system are time independent, one-dimensional integrals.

As the initial distribution function, a function was selected for which an exact solution was constructed [16]:

$$F(0, c) = \begin{cases} 0,56598 & 0 \leq c \leq 1,30286; \\ 1,41496(1,5 - 1,13980c) & 1,30286 \leq c \leq 1,77662; \\ 0 & 1,77662 \leq c < \infty. \end{cases}$$

The calculations were carried out as follows: In the initial moment the solution of system (27) was found for the assigned distribution function. From the obtained α , β , and γ values, the F^+ function was determined using (26), which together with the known function determined the right-hand side of (24). The distribution function at time $t = 0.1$ was found from the known derivative $\partial F / \partial t$, by the Euler method with 0.1 intervals. Analogous calculations were carried out for all other moments of time.

The integrals were calculated by Simpson's rule, with 0.05 intervals in the range 0 to 5. Calculations were made on the "strela" electronic digital computer. The results of the calculations are represented in the form of graphs in Figures 1, 2, and 3. The solid curves are for the exact solution, dashed curves for the solution by the proposed method with F^+ in the form (26), and dash-dot-dash curves represent the second approximation [$\gamma \equiv 0$, only conservation laws are fulfilled; see the first two equations in system (27)]. On the same graph, short dashed curves show the results of

calculations by the Krook model equation. Figure 1 represents the distribution function at time $t = 1$, and also the initial ($t = 0$), and Maxwell functions ($t = \infty$). Figure 2 shows the same functions multiplied by c^2 . The results of calculations show that the behavior of the distribution function from /107
the fourth approximation is very close to the exact solution.

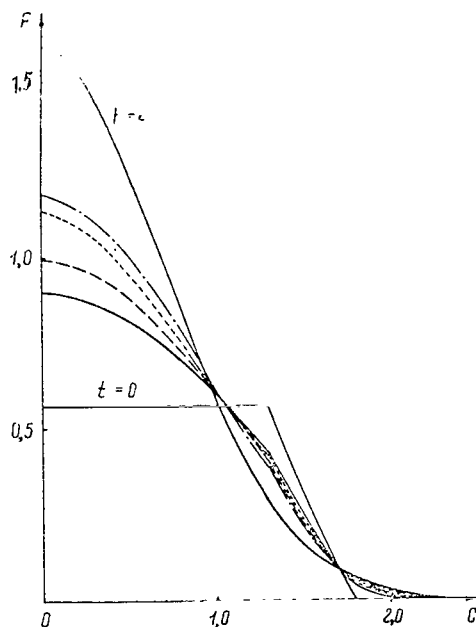


Figure 1. Distribution function $F(c)$ for $t=1$; --- second approximation; - - - fourth approximation; ----- Krook model; ——— exact solution.

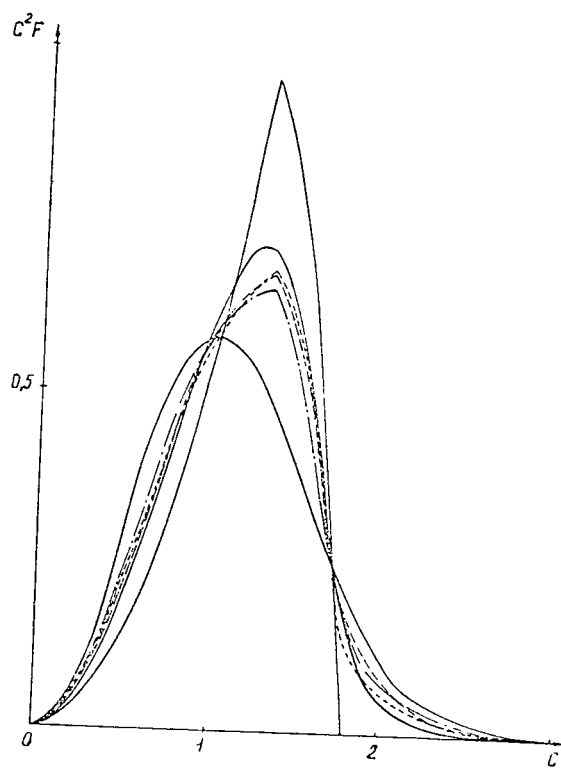


Figure 2. Function $c^2 F(c)$ for $t=1$.

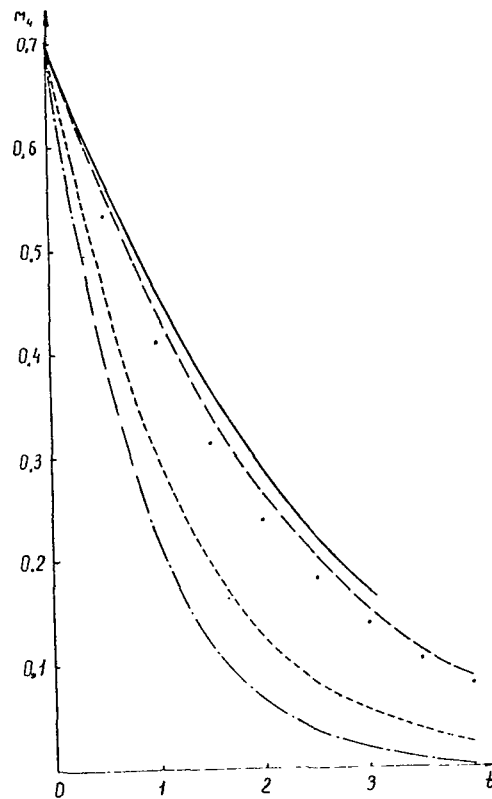


Figure 3. Changes of the fourth-order moment with time;

$$M_4 = \int_0^{\infty} c^6 (F^{(0)} - F) dc:$$

--- second approximation; - - - fourth approximation; Krook model;
 — exact solution; ●●●● Maxwellian molecule model.

Figure 3 shows changes of the first moment, which differs from the constant moment, the fourth order moment $Q_{iikk} = \int c^4 F d\vec{c}$ with time; along the ordinate axis the quantity

$$M_4 = \int_0^{\infty} c^6 (F^{(0)} - F) dc.$$

was plotted. The error in determining the considered fourth moment

Q_{iikk} from the fourth approximation does not exceed 1% of the exact value (the relaxation model gives a 7-8% error). When $t \approx 0$, the relative error in determining the M_4 integrals is 8%. For the relaxation model this error exceeds 50%.

For comparison the same figure (Figure 3) contains points which represent the values corresponding to Maxwellian molecules for gas of the same viscosity.

Attention is drawn to the significant difference between the results of the second and the fourth approximations, and also to the fact that the results of the second approximation are somewhat poorer than from the Krook model.

The indicated difference between the approximations is explained by the fact that in the approximation, a key factor is the relationship between nonzero collision integral moments, since the conservation laws in essence do not reflect the specificity of the Boltzmann collision integral. In fact, geometrically, the evolution of the distribution function and its tendency towards the equilibrium value indicates a continuous deformation of the $t = 0$ curve in Figure 1 to $t = \infty$. The conservation laws indicate that the deformation law must be such that the area bounded by the $c^2 F$ curve and the abscissa axis, as well as the area bounded by the abscissa axis and the $c^4 F$ curve (which is the same as the iteration moment of the first figure), must remain unchanged. The rate of curve deformation in the second approximation is independent of the accurate collision operator, and only in the fourth approximation is it taken into account in the integral sense.

Thus, the rate of approach of equilibrium will correspond in the moment sense to the Boltzmann collision operator, if above the conservation laws certain other nonzero collision integral moments are also taken into account. This also explains the fact that the Krook model is a better second approximation, since by replacing the collision frequency by a constant the properties of the Boltzmann collision integral are taken into account more fully (all second-order moment relationships are satisfied; see Section 3).

In conclusion, we note that the accepted collision frequency approximation was found to be quite satisfactory. Comparison of the collision frequency N_0 , determined from the initial distribution function, with the equilibrium value has shown that maximum deviation of N_0 from $N^{(0)}$ takes place when $c = 0$, and it does not exceed 5%. Because the Krook model with a

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problem, one would expect the collision frequency effect to be very small. Nevertheless, calculations were carried out with the accurate collision frequency. The results of calculations were found to be practically the same as those cited above.

7. Nonisotropic Relaxation of Boltzmann Gas in Homogeneous Space

The isotropic relaxation problem is not a characteristic one in the theory of rarefied gases. Actually, in the stream of rarefied gas, the distribution function does not possess isotropy in velocities, and it can have an extremely complex form. Nevertheless, in this section we also consider the simplified class of distribution functions which relax to the Maxwell distribution function. Results are given for the solution of the Cauchy problem for initial functions having axial symmetry in velocity space. The axial symmetry condition significantly simplifies the calculations and preserves the principal characteristics of the random distribution of molecular velocities (internal stresses and energy fluxes are not equal to zero in this case).

Numerical calculations were made for the distribution function, which can be represented by a linear combination of two Maxwell functions with mass velocities (the pseudo-shock problem [19]):

$$F_0 = F(0, \vec{c}) = a_1 \theta_1^{\frac{3}{2}} e^{-\theta_1 [(u - U_1)^2 + V^2]} + a_2 \theta_2^{\frac{3}{2}} e^{-\theta_2 [(u + U_2)^2 + V^2]}, \quad V^2 = v^2 + w^2, \quad (28)$$

here u , v , and w are components of the molecular velocity vector \vec{c} . Constants a_1 , a_2 , U_1 , U_2 , θ_1 , θ_2 are related by the conditions of constant density and temperature and the absence of mass velocity:

$$\left. \begin{aligned} \int F_0 d\vec{c} &= \int F^{(0)} d\vec{c}; \\ \int c^2 F_0 d\vec{c} &= \int c^2 F^{(0)} d\vec{c}; \\ \int u F_0 d\vec{c} &= 0. \end{aligned} \right\} \quad (29)$$

Conditions (29) lead to the following relationships for $a_1, a_2, U_1, U_2, \theta_1, \theta_2$:

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$$\begin{aligned} a_1 + a_2 &= 9/4\sqrt{2}; & a_1 U_1 - a_2 U_2 &= 0; \\ a_1 \left(U_1^2 + \frac{3}{2\theta_1} \right) + a_2 \left(U_2^2 + \frac{3}{2\theta_2} \right) &= \frac{27}{8\sqrt{2}}. \end{aligned}$$

The form of the initial function permits easy calculation of all of the necessary distribution function moments. In particular

$$\begin{aligned} P_{11}(0) &= \int u^2 F_0 d\vec{c} = a_1 \pi^{\frac{3}{2}} \left(U_1^2 + \frac{1}{2\theta_1} \right) + a_2 \pi^{\frac{3}{2}} \left(U_2^2 + \frac{1}{2\theta_2} \right); \\ S_1(0) &= \int u c^2 F_0 d\vec{c} = a_1 \pi^{\frac{3}{2}} U_1 \left[U_1^2 - U_2^2 + \frac{5}{2} \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right) \right]. \end{aligned}$$

If $U_1 = U_2$ in F_0 , then $a_1 = a_2, \theta_1 = \theta_2 = \theta$, i.e., the initial function is symmetric with respect to the $u = 0$ plane, thermal flux $2S_1$ is equal to zero, and, for the stresses at the initial moment, the following equation holds:

$$\frac{p_{11}(0)}{p} = 2 \left(1 - \frac{1}{\theta} \right); \quad p_{11} = P_{11} - p, \quad (30)$$

where p is gas pressure; p_{11} is the excess pressure caused by deviation from equilibrium.

Equation (30) shows that in the symmetrical case the excess pressure cannot exceed the gas pressure by more than a factor of two (when $\theta \rightarrow \infty$, the initial function becomes a δ -function with limiting values $U_1 = U_2 = \sqrt{1.5}$).

The initial function in the form (28) is also convenient in that it permits calculation of the collision frequency

$$\begin{aligned} N_0 &= \frac{2}{9\pi} \int F(0, c_1) |\vec{c} - \vec{c}_1| d\vec{c}_1 = \\ &= \frac{4\sqrt{2}}{9} \left\{ \frac{a_1}{\sqrt{\theta_1}} N^{(0)}(\lambda_1) + \frac{a_2}{\sqrt{\theta_2}} N^{(0)}(\lambda_2) \right\}; \\ \lambda_1 &= \sqrt{\theta_1 [(u - U_1)^2 + V^2]}; \quad \lambda_2 = \sqrt{\theta_2 [(u + U_2)^2 + V^2]}, \end{aligned}$$

where $N^{(0)}$ is defined by formula (25).

Figure 4 represents the Maxwell and the initial (dashed curve) distribution functions for $U_1=0.25$; $U_2=2.75$; $\theta_1=1.79$; $\theta_2=2.75$ and the appropriate collision frequencies. In spite of large differences in the distribution functions, the corresponding collision frequencies are close. Considering this fact and the fact that the collision frequency itself affects the solution relatively little, we can assume, as in Section 6, that the collision frequency is defined by formula (25). /111

The relaxation problem with an initial function in form (28) was solved for the approximating equation of the incomplete third approximation, i.e., for equation (24) with F^+ in the form:

$$F^+ = F^{(0)} (1 + \alpha + \beta u + \gamma c^2 + \delta u^2 + \varepsilon u c^2).$$

In determining the α , β , γ , δ , and ε coefficients when

$$\psi = 1, u, c^2, u^2, u c^2$$

the moment relationships (27) give a system of linear algebraic equations with constant coefficients. The right-hand sides of these equations

$$= \int \psi N^{(0)} (F_- - F^{(0)}) d\vec{c} + \frac{2}{9\pi\sigma} \int (\psi' - \psi) F F_1 g d\sigma d\vec{c} d\vec{c}_1$$

change with time and tend to zero in the course of the establishment of equilibrium. The collision integral moments for the collision invariants are equal to zero. For ψ , equal to u^2 , $u c^2$, one can integrate over the collision parameters and obtain the quantities in the expression (20) with an accuracy equivalent to the magnitude of the scaling factor. Axial symmetry allows the number of quadratures to be decreased to four. As a result of these transformations, the following is obtained:

$$\left. \begin{aligned}
I_{11} &= \frac{4}{9} \int \left\{ \left[-u^2 + uu_1 + \frac{1}{4} (u-u_1)^2 \right] qA(k) + \right. \\
&\quad \left. + \frac{1}{3} q^3 B(k) \right\} FF_1 VV_1 du du_1 dV dV_1; \\
I_{1jj} &= \frac{4}{9} \int \left\{ \left[-uc^2 + \frac{1}{4} (u+u_1)(c^2 + c_1^2) \right] qA(k) + \right. \\
&\quad \left. + \frac{1}{3} (u+u_1) q^3 B(k) \right\} FF_1 VV_1 du du_1 dV dV_1; \\
V &= \sqrt{v^2 + w^2}; \quad q = \sqrt{(v-u_1)^2 + (V+V_1)^2}; \quad 0 \leq k = \frac{4VV_1}{q} \leq 1; \\
V(k) &= \int_0^{\pi/2} (1-k\cos^2\psi)^{1/2} d\psi; \quad B(k) = \int_0^{\pi/2} (1-k\cos^2\psi)^{3/2} d\psi.
\end{aligned} \right\} \quad (31)$$

The calculations were conducted in the same manner as was used in solving the isotropic relaxation problem. All of the integrals were calculated by 112 Simpson's rule within the range $-5 < u < 5$, $0 < V < 5$ in 0.25 increments. The selected grid for u , V allowed varying the problem parameters within broad limits without loss of accuracy.

Calculations were made using complete moments of collision integrals (31) and a linear approximation I_{11} , I_{1jj} by the method proposed in Section 5 of this work, i.e., using (23).

The results of the calculations are represented in the form of graphs in Figures 5-9. Figure 5 represents the changes in the profile $V=0$ of the distribution function with time for the symmetric case:

$$U_1 = U_2 = \frac{1}{\sqrt{2}}, \quad \theta_1 = \theta_2 = \frac{3}{2}, \quad \frac{p_{11}(0)}{p} = \frac{2}{3},$$

calculated for comparison with the results of F. G. Cheremisin [17]. The dashed curve corresponds to the solution obtained with the Krook equation, and the dashed curve with x 's corresponds to the F. G. Cheremisin solution. Comparison of the results of this work [17] shows that significant differences in distribution function behavior occur only in the region of small velocities. The attenuation of p_{11} with time with an accuracy to the calculation errors, as in [17], corresponds to the Krook model (or

to the Maxwellian molecules), i.e.,

$$p_{11} = p_{11}(0)e^{-0.8t}. \quad (32)$$

Figure 6 represents the distribution function behavior in the $V = 0$ cross section; this is the same as for the symmetric case, but with significantly greater deviation of the initial function from the equilibrium function

$$U_1 = U_2 = 1, \quad \theta_1 = \theta_2 = 3, \quad \frac{p_{11}(0)}{p} = \frac{4}{3}.$$

The additional stress attenuates by essentially the same law (32).

This characteristic of the symmetric case is explained by the fact that the linear correction in approximating the integral by the method described in Section 5, which for the initial function (28) is calculated analytically, is comparable to the error in Euler method calculations.

Let us note that in the symmetric case the solutions of the approximating equations of the second and third approximations coincide.

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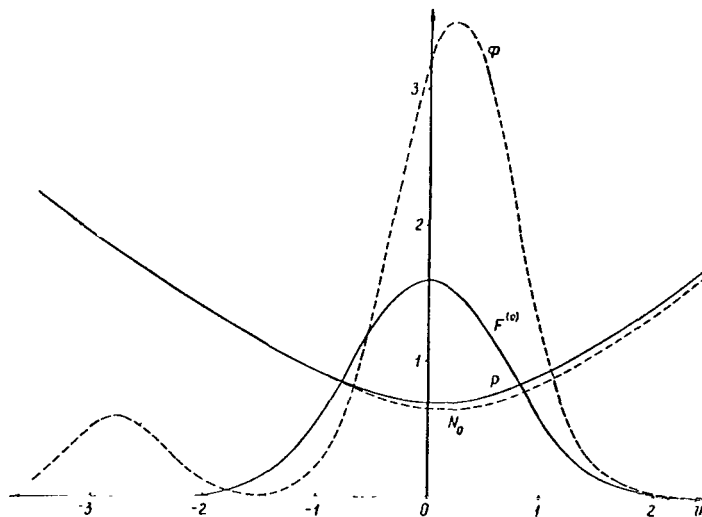


Figure 4. Distribution functions Φ (--- initial) and $F^{(0)}$ (— Maxwellian) and the corresponding collision frequencies N_0 and P ; $V = 0$ cross section.

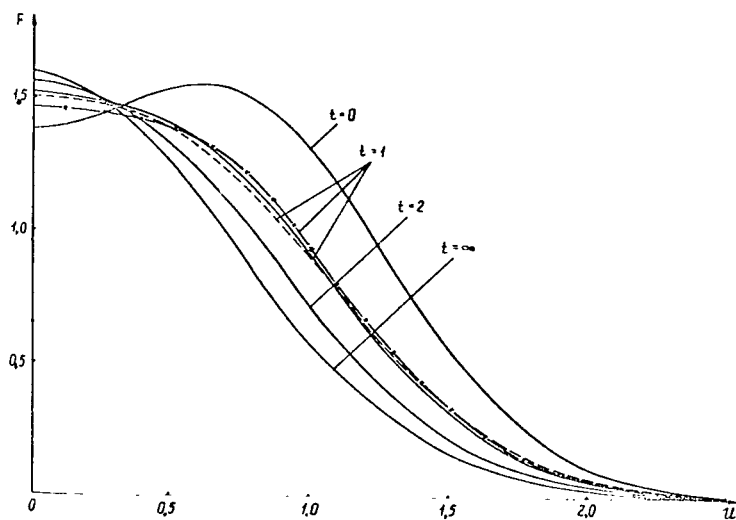


Figure 5. Changes in the distribution function ($V = 0$) with time; —x— Cheremisin's solution; ---solution from the Krook equation;

$$U_1 = U_2 = \frac{1}{\sqrt{2}}, \quad \frac{p_{11}(0)}{p} = \frac{2}{3}.$$

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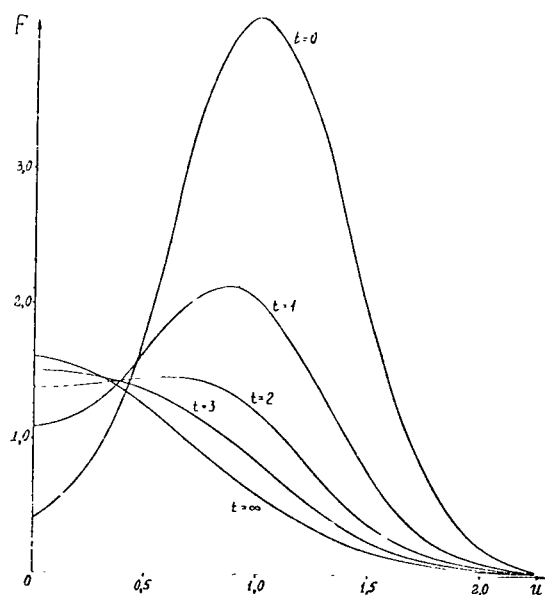


Figure 6. Distribution function ($V = 0$) for the case $U_1 = U_2 = 1$;

$$\frac{p_{11}(0)}{p} = \frac{4}{3},$$

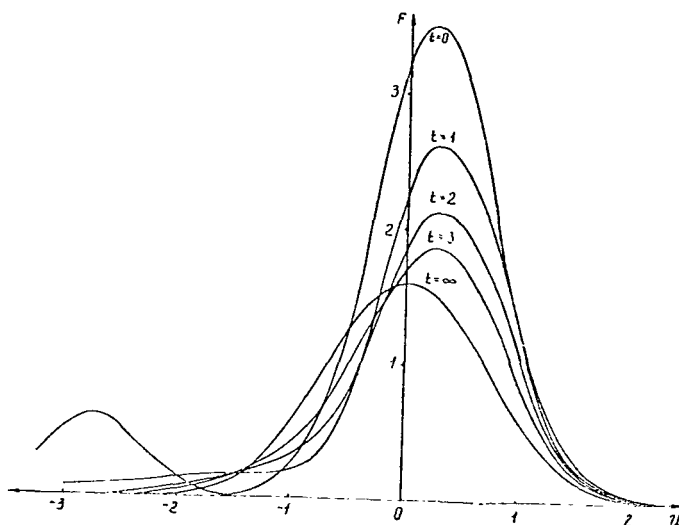


Figure 7. Distribution function behavior ($V = 0$) in the problem of nonisotropic relaxation (asymmetric case).

The problem of symmetric pseudo-shock was considered earlier [19]. Some differences in the qualitative behavior of the distribution function appeared, apparently resulting from the fact that in [19] calculations were made with insufficient accuracy (density and temperature in the time interval from 0 to 1 differed from the precise values by approximately 10%).

The case of asymmetric initial distribution functions is of significantly greater interest. Figures 7-9 represent the results of calculations of the variations $U_1=0.25$, $U_2=2.75$, $\theta_1 \approx 1.79$, $\theta_2=2.75$. Here at the initial moment:

$$\frac{p_{11}(0)}{p} \approx 0,9; \quad \frac{S_1(0)}{\rho(2RT)^{3/2}} \approx 1,6.$$

The initial function, as is apparent, differs significantly from the equilibrium function.

The evolution of the distribution function is represented in Figure 7 ($V=0$ cross section). Attention is drawn to the fact that, in contrast to the above-mentioned symmetric case, the behavior of F does not correspond to the distribution function behavior according to the Krook equation. According to the Krook model, the distribution function for each value

of the velocity relaxes independently of the remaining velocities; the obtained solution, however, indicates the complex interaction of particles having different velocities.

The attenuation of the excess pressure p_{11}/p and thermal flux $\bar{S}_1 = S_1/\rho(2RT)^{3/2}$ is represented in Figures 8 and 9. The attenuation of p_{11}/p and S_1 is much faster than for Maxwellian molecules (dashed curves); attenuation of S_1 is slower than that obtained in the Krook model (dash-dot-dash).

All of the results presented thus far were obtained without the use of the approximation for the collision integral moments by the method described in Section 5 of this work. Computation time for one variant, using the BESM-6 computer for time intervals of from zero to four, was approximately 5.5 hours. The approximation of the collision integral moments in the linear approximation reduces the computation time of a single variant to forty-five seconds. Corresponding results for the moments were plotted as points in Figures 8 and 9. For the logarithmic derivatives $d(\ln p_{11})/dt$, $d(\ln S_1)/dt$ at the initial moment, the exact values are equal to -1.08 and -0.714 respectively; the Maxwellian model gives $-4/5$ and $-8/15$, while the linear approximations give -1.16 and -0.75 .

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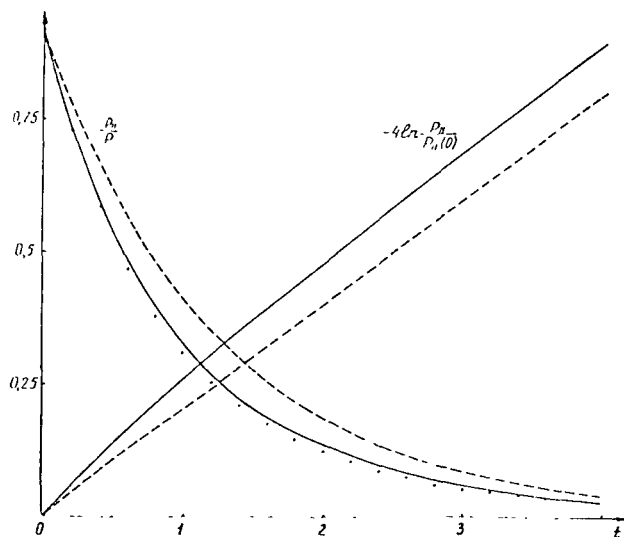


Figure 8. Attenuation of the excess pressure p_{11}/p ; --- Maxwell model; — proposed method; ●●● proposed method with the approximation of the collision integral moments.

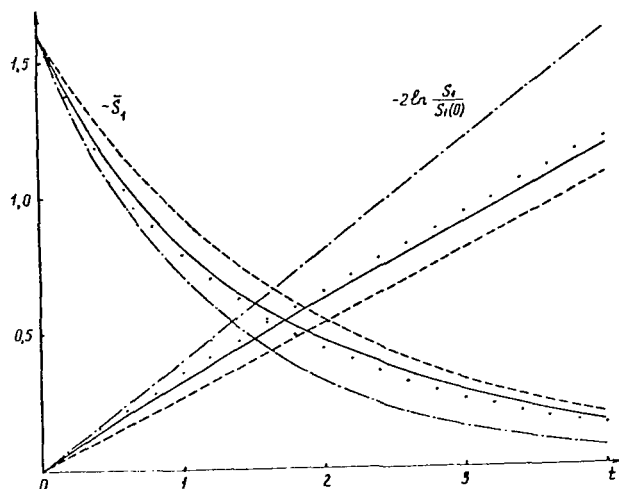


Figure 9. Attenuation of thermal flux; --- Maxwell model of molecules; — proposed method; ••• method proposed with the approximation of collision integral moments; -·-·- Krook model.

Thus, the approximation of collision integral moments, as well as the linear approximation, insures an acceptable accuracy and decreases the computer time necessary significantly (in the considered problem by a factor of more than 400).

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Conclusions

The methods developed in this work for the approximation of collision integrals, based on satisfying the moment integral relationships, choosing approximating formulas for the return collisions integral and collision frequency, and collision integral approximating moments, reduced the Boltzmann equation to a series of approximating equations. Each approximating equation has an approximate operator for return collisions and collision frequency, which depends only on the distribution function moments, i.e., the approximate collision operator in this sense is analogous to Krook equation relaxation operator.

Any method for numerical solution of the Boltzmann equation (including the Monte Carlo methods) is also applicable to the approximating equation. However, the specific structure of the collision integral, which permits

the construction of the numerical solution without retaining the distribution function, should also be used in choosing the numerical methods. From this standpoint, the discrete velocities method is the most promising.

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MODELS FOR THE INTERACTION OF RAREFIED GAS
WITH A SURFACE

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In the course of the investigation and calculation of the flow of a rare- /119
fied gas, for which the boundaries are in the form of solid surfaces, it
is necessary to know the recoil velocity of the molecules from the surface.
However, the calculation of the distribution function for recoil
particles presents significant difficulties due to insufficient
knowledge of the recoil phenomenon and due to the lack of
knowledge of the surface properties themselves. Even in the case of
isolated recoil of the gaseous atoms from a solid surface, the analytical
expression for the distribution function of the recoiled particles may be
written only for the smooth sphere model [1]; in the case of other
interaction potentials at best an extremely complex expression can be
derived for the momentum and energy exchange coefficients [2]. Taking
into account the collective nature of the interaction, the determination
of the total energy, momentum and other macroscopic properties for the
recoil molecule is possible only by the numerical method. It should
be noted, however, that the volume of calculations is so great, that it
imposes limitations on the interaction model.

In this work, various theoretical models for the interaction of
gaseous atoms with solids at energies of ~ 10 eV are discussed. The
surface is modeled by a one- and three-dimensional aggregate of atoms with
different initial conditions and lattice parameters.

In calculating the accommodation coefficients, the direct inte-
gration of the equations of motion of gaseous molecules and atoms
in the crystal lattice of the solid is used. An analysis of the advantages
and the drawbacks of the models, as well as the possibilities of the
analytical solutions in a one-dimensional case, is given. The dependence of
the energy, the normal and the tangential momenta accommodation coefficients
on the collision parameters is obtained.

1. Accommodation coefficients. The calculation method

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All theoretical works on the interaction of gas atoms with a surface

are generally devoted to the calculation of momentum and energy exchange coefficients or the equivalent accommodation coefficients.

Knudsen [3] was the first to utilize the formula $\alpha = T_r - T_g / T_r - T_g$, [sic] where T_g is the gas temperature, T_s is the surface temperature, T_r is the temperature of the recoiled gas, which corresponds to the quantity characterizing the energy transfer from the gas to the surface of the solid - the temperature accommodation coefficient. If one considers a process in which each molecule collides with the surface only once, one can determine the energy (kinetic energy) accommodation coefficient and the momentum accommodation coefficient from the following formula

$$\alpha = 1 - \frac{v^2}{v_g^2}; \quad \alpha_n = 1 - \frac{v_n}{v_{ng}}; \quad \alpha_\tau = 1 - \frac{v_\tau}{v_{\tau g}},$$

where the subscript n refers to the normal component of the \vec{v} vector, and τ refers to the tangential vector component.

The first attempt to calculate the accommodation coefficient α by classical mechanical methods, based on the well-known properties of gas atoms and a solid surface with the use of the simplest model of solid spheres was made by Baule [4]. However, this model raises some objections since the presence of the surface is in no way taken into account. In a study by R. G. Barantsev [1], the interaction of gas particles having an energy of 5 - 10 eV and a relative mass $\mu = M/m < 1$, with the assumption of absence of an absorption layer was considered for the case of paired interactions. For a simple isolated recoil, the directional distribution of the reflected particles was obtained for the case of dense packing of surface atoms. The energy and momentum exchange coefficients were also calculated. Apparently, one can obtain a sufficiently close description of the real interaction if one considers nonlinear terms in the expression for the forces of interaction of both a gas particle with the surface atoms in the lattice and among the atoms within the lattice. A one-dimensional model was used in [5, 6, 7], where the solid was approximated by a linear chain of quasi-elastically bound atoms, which are initially

immobile. The oncoming atom moves along the axis of the chain, so that the collision is frontal. Assuming that the force of interaction with the first atom in the chain is a known function of time, after some transformations one can obtain a single resultant equation for the relative displacement of the first pair of colliding atoms instead of a system of equations for motion of the chain. Goodman [8] considered a three-dimensional lattice, for which he calculated the reaction to a force applied perpendicular to the lattice surface to a specific (initial) atom. The equations of motion for a three-dimensional infinite lattice were written analogously to a one-dimensional case and are solved using the Fourier transform. In the work [9], accommodation coefficients for argon molecules on a cold tungsten surface were calculated. In this problem, the initial gas molecule trajectory had a random direction relative to the surface. /121

However, with the use of a three-dimensional model, an analytical approximate solution (not to mention an accurate solution) can be obtained only in exceptional cases. The significance of numerical calculations on an electronic digital computer increases due to the possibility of creating model interactions, which in principle would be satisfactory for taking many interaction parameters into account. For example, in [10], a large volume of numerical calculations of the classical trajectory of gas particles having energies of 0.1 - 15 eV near the surface of a solid crystalline body were performed.

2. Choice of potential. Interaction with crystals

The potential function $\varphi(r) = \infty, r < \sigma; \varphi(r) = 0, r > \sigma$ represents solid impermeable spheres of diameter σ . This model is frequently used in calculations due to its simplicity. However, it gives only a rough idea of the strong briefly acting repulsive forces, since it is well known that two molecules repel each other upon approach at sufficiently close distances, but attract each other when they are far removed. The Lennard-Jones potential [6 - 12] is a function which is frequently used for the intermolecular potential energy

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1)$$

This function gives sufficiently simple and realistic representation of the interaction among spherical nonpolar molecules, and in further /122 calculations we shall make use of this particular potential. The parameters σ and ϵ , having dimensions of length and energy respectively, are constant; they characterize the chemical differences of the colliding particles. The ϵ quantity is the r value at which $\varphi(r) = 0$; ϵ is the maximum energy of attraction which is achieved when $r = \sqrt[6]{2\sigma}$.

In the case of paired interaction of gas molecules and solids, the interaction potential is expressed by a single function of the distance between these particles. In the case of collective interaction (two- or three-dimensional models), the potential at a given point A near the surface consists of the potentials of interaction with all the lattice surface nodes, i.e.,

$$\begin{aligned}\varphi(A) &= \varphi(r_0) + \sum_{p \neq 0} \varphi(r_p); \\ \varphi(A) &= \varphi(r_0) + \sum_{p, q \neq 0} \varphi(r_{p,q})\end{aligned}$$

in the two- and three-dimensional models respectively.

Here r_0 is the distance to the target atom and p, q are the numbers of its neighbors. Without diminishing the generality, but only for simplifying computations we shall consider in the future, the normal frontal collisions, and the expressions for potential $\varphi(A)$ will acquire the following form

$$\left. \begin{aligned}\varphi(A) &= \varphi(r_0) + 2 \sum_{p=1}^{\infty} \varphi(r_p); \\ \varphi(A) &= \varphi(r_0) + 4 \sum_{p=1}^{\infty} \varphi(r_p) + 4 \sum_{\substack{p>0 \\ q>0}} \varphi(r_{p,q});\end{aligned}\right\} \quad (2)$$

$r_p^2 = x^2 + (pa)^2$; $r_{p,q}^2 = x^2 + (p^2 + q^2)a^2$; x is normal with respect to the surface.

However, upon replacing $\varphi(r)$ by a potential which is close to the real potential (for example, the Lennard-Jones

potential) (6 - 12), it becomes difficult to compute analytically the sums in these expressions. Moreover, there is no need for this since it is sufficient to have the evaluation of the forces of interaction from the far-removed surface atoms. Referring all of the distances to the lattice spacing and assuming σ to be constant in the Lennard-Jones potential and equal to a , function $\varphi(r)$ for this potential will be replaced by the function $\varphi(r^*) = 1/r^{*12} - 1/r^{*6}$, where $r^{*2} = p^2 + s^2$; $r_{p,q}^{*2} = p^2 + q^2 + s^2$; $s = x/a$ is the relative distance of a gas atom from the target, with the accuracy equivalent to the value of the constant coefficient. /123

Thus, at a fixed point A, the potential $\varphi(A)$ is a function only of p in the two-dimensional case and a function of two variables p, q in the three-dimensional case. Let us consider the first case.

If we designate the partial sum of the series $\sum_{p=1}^{\infty} \Psi(p)$ through S_p ,

then the remainder $R_p = \Psi(p+1) + \Psi(p+2) + \dots$ as a result of convergence of the series satisfies the following inequality

$$\int_{p+1}^{\infty} f(p)dp < R_p < \int_p^{\infty} f(p)dp, \quad (3)$$

where $\varphi(r_p) \equiv \Psi(p)$ and $f(p)$ in the improper integral $\int_p^{\infty} f(p)dp$ is a monotonically decreasing function of p , which acquires the values $\Psi(1), \Psi(2), \Psi(3), \dots$ when $p = 1, 2, 3, \dots$

For the specific case of $2p$ neighbors surrounding the target atom, the summed potential is calculated at any fixed point near the surface. The inequality (3) allows evaluation of the error introduced by neglecting the effect of the surface atoms which are removed even further. The integrals in (3) for the Lennard-Jones potential are evaluated analytically. In the future only the second of these is needed

$$\begin{aligned} \int_p^{\infty} f(p)dp = & \left(\frac{63}{256 s^{11}} - \frac{3}{8 s^5} \right) \frac{\pi}{2} - \frac{p}{10 s^2 (p^2 + s^2)^5} - \frac{9p}{80 s^4 (p^2 + s^2)^4} - \\ & - \frac{63p}{480 s^6 (p^2 + s^2)^3} - \frac{63p}{384 s^8 (p^2 + s^2)^2} - \frac{63p}{256 s^{10} (p^2 + s^2)} + \frac{p}{4 s^2 (p^2 + s^2)^2} + \\ & + \frac{3p}{8 s^4 (p^2 + s^2)} + \left(\frac{3}{8 s^5} - \frac{63}{256 s^{11}} \right) \operatorname{arctg} \frac{p}{s}. \end{aligned}$$

During the interaction with the surface, the evaluation of the second term in the expressions for the potential function (2) is analogous to the two-dimensional model ($q = 0$), while the last term can be represented in the following form

$$\sum_{p=1}^{\infty} \left[\sum_{q=1}^{\infty} \varphi(r_{p,q}) \right] = \sum_{p=1}^{\infty} S_{p,q}.$$

In it the evaluation of (3) is valid upon replacement of $f(p)$ by $S_{p,q}$ 124 and assuming that the internal sum is calculated precisely. If one designates the remainder of the inner series by R_q in an approximate computation of the latter, R_q then satisfies the inequality

$$\int_{q+1}^{\infty} \varphi(r_{p,q}) dq < R_q < \int_q^{\infty} \varphi(r_{p,q}) dq.$$

As a result the error increases and for R_p the upward evaluation will already be valid

$$R_p < \int_p^{\infty} \left[\sum_{q=1}^q \varphi(r_{p,q}) \right] dp + \sum_p R_q. \quad (4)$$

With assigned p and q values, with p constant, the R_q value is estimated. Similarly for all other p values. Summing these upper limits, we obtain the second term in expression (4). After calculating the partial sum for q , the integral in the first term is computed by the ordinary method (it is also possible to exchange the summation and the integration).

Calculations were performed for the relative error ΔR in the interaction potential as a function of a number of atoms neighboring the target atom which were taken into account. Some of the evaluations are given in Table 1. In the three-dimensional model, the relative error is somewhat higher than in the two-dimensional model, and it is several times larger for a small number of neighbors, however, the error decreases with an increase in the number of neighboring atoms so intensely, that for practical purposes a sufficient accuracy is achieved when an identi-

cal number of neighbors is taken into account in both the two- and three-dimensional cases.

TABLE 1.

$p - q$	$s = 0,5$		$s = 1,0$		$s = 1,5$		$s = 2,0$	
	ΔR_p	ΔR_{pq}	ΔR_p	ΔR_{pq}	ΔR_p	ΔR_{pq}	ΔR_p	ΔR_{pq}
1	$0,5 \cdot 10^{-4}$	$0,9 \cdot 10^{-4}$	0,277	0,434	0,180	0,304	0,269	0,423
2	$0,3 \cdot 10^{-5}$	$0,4 \cdot 10^{-5}$	0,032	0,047	0,032	0,047	0,073	0,106
3	$0,4 \cdot 10^{-6}$	$0,5 \cdot 10^{-6}$	0,005	0,007	0,007	0,009	0,020	0,026
5	$0,3 \cdot 10^{-7}$	$0,4 \cdot 10^{-7}$	$0,5 \cdot 10^{-7}$	$0,8 \cdot 10^{-7}$	$0,7 \cdot 10^{-7}$	$0,9 \cdot 10^{-7}$	0,003	0,003
10	$0,1 \cdot 10^{-8}$	$0,1 \cdot 10^{-8}$	$0,2 \cdot 10^{-8}$	$0,2 \cdot 10^{-8}$	$0,3 \cdot 10^{-8}$	$0,1 \cdot 10^{-8}$	$0,1 \cdot 10^{-8}$	$0,1 \cdot 10^{-8}$
20	$0,4 \cdot 10^{-10}$	$0,4 \cdot 10^{-10}$	$0,5 \cdot 10^{-6}$	$0,5 \cdot 10^{-6}$	$0,8 \cdot 10^{-6}$	$0,9 \cdot 10^{-6}$	$0,3 \cdot 10^{-7}$	$0,3 \cdot 10^{-7}$

Comparing the results with the evaluation of forces from far-removed atoms on the surface during isolation of the zone of strong interactions, we note that the results coincide qualitatively, i.e., the dominating effect in the collision process of gas atoms with the wall results only from the interaction of the nearest neighbors to the target atom, the number of which depends primarily on the potential parameters and for known potentials (including the Lennard-Jones function), taking into account the approximate values of the parameters themselves, does not exceed two to three. However, the zone of free motion depends primarily on the velocity of the oncoming gas molecules [2]. /125

3. System of determining parameters. Formulation of the problem

On the edge of a surface (or at the end of a one-dimensional chain) let us select an atom and call it the initial atom. The coordinate system (Figure 1) will be defined in such a way that its origin coincides with the equilibrium position of the initial atom, while the axis X_3 will be directed normal to the surface (or along the axis of the chain). We shall assume that the crystal lattice is of the simple cubic type. The interactions between the atoms in such a crystal are described by a harmonic potential with the force constant κ ; the magnitude of the interaction force is proportional to the relative displacement of the atoms. Let us also assume that the initial atom can be bound to its nearest neighbors through a potential $\phi_1(r)$, different from the harmonic potential. This, so to speak, simulates the interaction with the adsorbed atom. The interaction of the oncoming particle with the initial atom, as

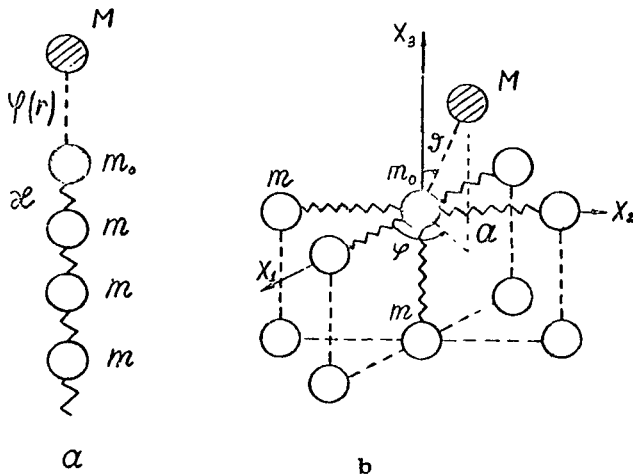


Figure 1. Interaction scheme:

- a- one-dimensional chain;
- b- three-dimensional crystal model.

well as with other surface layer atoms in the lattice is determined by a potential $\varphi(r)$ in the form of (1) or by a harmonic potential with the force constant κ_0 . In the latter case, it is convenient to introduce a parameter $\beta = \kappa_0/\kappa$; $\gamma = \beta(1 + \mu)/\mu$, where $\mu = M/m$ is the ratio between the masses of gas and wall atoms. In addition to the potential parameters and the ratio of the atomic masses, an individual interaction event is also characterized by the following parameters: initial macroscopic velocity of the gas atoms, determined by the vector \vec{v} , whose spatial orientation is defined by the θ angle (with the normal) and ϕ (azimuth), the spatial position of the gas atom (r, ϑ, Ψ) at the initial time $\tau = 2\sqrt{\kappa/m} t = 0$, displacement \vec{r}_{pqs} and the velocity \vec{u}_{pqs} of the lattice atoms. The lattice spacing a and the distribution function $f(\vec{U})$ for the characteristic velocities of gas atoms are also stipulated. It is convenient to introduce into the initial conditions the parameter α^0 , defined as the ratio of the depth of the potential curve $\varphi(r)$ to the bond energy in the lattice $1/2 \kappa \sigma^2$. The kinetic energy of gas particles will be characterized by the parameter ϵ from the expression $Mv_0^2 = 2\epsilon$; all linear dimensions are expressed in terms of the lattice spacing, which in the case at hand can be taken as equal to σ .

The resulting system of equations describing the motion of the entire interacting set of particles may be written as follows:

$$\left. \begin{aligned} M \ddot{\vec{r}}_{p,q} &= -\sum \frac{d\varphi(r_{p,q,0})}{dr_{p,q,0}} \frac{\vec{r} - \vec{r}_{p,q,0}}{r_{p,q,0}}; \\ m \ddot{\vec{r}}_{p,q,0} &= \frac{d\varphi(r_{p,q,0})}{dr_{p,q,0}} \frac{\vec{r} - \vec{r}_{p,q,0}}{r_{p,q,0}} + F_{p,q,0}; \\ m \ddot{\vec{r}}_{p,q,s} &= F_{p,q,s}. \end{aligned} \right\} \quad (5)$$

After the introduction of the above-mentioned dimensionless parameters, any interaction model can be obtained in both three- and in one-dimensional form. Here $F_{p,q,s}$ is the force acting on the lattice atoms designated p, q, s .

The value of the parameter l is determined by the energy of the oncoming atom and for a velocity 6-10 km/sec is of the order of $10^2 - 10^3$ when $M \approx 10^{-23}g$, $\epsilon \approx 10^{-1} - 10^{-2}$ eV. On the basis of the fact that the bond energy $1/2 \alpha \sigma^2$ is of the order of several electron volts, α^0 will be of the order of $10^{-2} - 10^{-3}$. The displacement of lattice atoms at the initial time may attain values from -0.1 to +0.1 and velocities which do not disrupt the intactness of the lattice (the condition of the equality of potential energy of the lattice bond and the kinetic energy of the vibrational motion of an individual atom). The stipulation of the initial conditions in combination with the system of equations (5) completes formulation of the problem. /127

4. One-dimensional lattice model. Analytical and numerical solution

In spite of the apparent simplicity and unreality of the one-dimensional interaction model, it is this very model which made it possible to obtain the first results both for analytical and numerical solutions.

In references [5, 6, 7], cited above, the one-dimensional model was investigated in considerable detail. The only assumption which was made was an absence of thermal motion of the atoms in the chain prior to the onset of interaction. The possibility of taking thermal oscillations of the lattice atoms into account in a one-dimensional case was noted in [11]. The resulting system of equations describing the phenomenon was transformed in the usual way into a first-degree system, after which the introduction of a generating function of

the form $G(\rho, \tau) = \sum_{s \geq 1} x_s(\tau) \rho^s$ resulted in $x_1(\tau)$ for the relative displacement of the oncoming gas atom and the first atom in the chain equation

$$\frac{d^2 x_1(\tau)}{d\tau^2} = -\frac{\gamma}{4} x_1(\tau) + \frac{\beta}{2} \int_0^\tau \frac{J_2(t)}{t} x_1(\tau-t) dt + [J_1(\tau) + J_3(\tau)] x_2(0) - \sum_{s \geq 3} (-1)^s [J_{s-3}(\tau) - J_{s+1}(\tau)] x_s(0),$$

where $J_s(\tau)$ is the Bessel function and $x_s(0)$ are the initial atom displacements in the lattice.

In the case of zero initial perturbations, we can apply the Laplace transform to this equation and all the calculations can be performed analytically. In our case, finding the reverse transformation analytically produces an effect only when $\frac{1-\sqrt{1+2\beta}}{(1+\beta)^2} = \beta^*$, whereas when $\beta \leq \beta^*$ it leads far more rapidly to the numerical finding of the original. Thus the original is computed in a combined procedure; this means that when $\beta > \beta^*$, integration¹²⁸ is performed in a complex plane along the known contour, and when $\beta \leq \beta^*$ the expansion coefficient

$$x_1(\tau) = x_1(-\frac{1}{\beta} \ln \cos \vartheta) = \sum_{\nu=0}^{\infty} C_\nu \sin(2\nu + 1)\vartheta,$$

is computed in the form

$$\begin{aligned} C_0 &= \frac{1}{\pi} \circ F_1(\sigma); \\ C_0 + C_1 &= \frac{1^2}{\pi} \circ F_1(3\sigma); \\ &\dots \end{aligned}$$

where $F_1(\sigma)$ is the Laplace transform for $x_1(\tau)$. The velocity of the oncoming particle is then expressed through $x_1(\tau)$ from the relationship

$$x(\tau) = x(0) - \frac{\beta}{2\mu} \int_0^\tau x_1(t) dt,$$

while the energy transfer to the chain is expressed in an ordinary manner.

On the basis of calculations, performed under the assumption of constant values of the initial displacements and velocities of lattice atoms, certain conclusions can be drawn:

1) the interaction depends strongly on the μ and β parameters (with an increase in μ the number of lattice atoms participating in a collision event increases, while an increase in β gives the opposite effect); in practice, oscillations of lattice atoms with number $s = 10$ no longer affect the relative displacement of a gas atom from the first atom in the chain;

2) a characteristic of the interaction of a gas atom with the initially oscillating lattice is the presence of temporary capture of the gas atom with subsequent reflection of the two - three oscillations together with the lattice;

3) accommodation coefficients, calculated for the case when the atom is reflected without capture, i.e., immediately after the first oscillation, have smaller values than in the case of the same collision parameters but with an initially quiescent lattice.

Further calculations were made for chains with altered initial conditions. It was assumed that displacements from the equilibrium position and the velocities of all lattice nodes are random in magnitude and direction, however, they are within the limits of the admissible values for displacements not exceeding approximately 0.1 of the inter-atomic distance in the lattice, while the kinetic energy during the oscillations of the lattice atom does not exceed the bond energy. Then, averaging of the results of calculations with various initial conditions for a given interaction energy yields the mean /129 accommodation coefficients for normal momentum and energy. The comparison of the obtained values of coefficients with the available results, where the averaging was not conducted, show that the effect of the presence of starting perturbations is preserved independently of the length of the chain, while the exchange coefficients at various starting conditions are basically close to the average values. The length of the chain has an effect on the exchange only at low energies of interaction, while for the gas atom velocity range of practical interest one can limit oneself with great accuracy by taking only five or six atoms in the linear model into account. It follows from the calculations that light gas particles are basically scattered with low accommodation, while during the interaction of heavy atoms the coefficients α_n and α are close to unity, so that at

low energies capture of a gas atom is possible. In the latter case, the gas atom may undergo oscillations near the surface for a quite long period of time or be captured immediately after the first oscillation.

TABLE 2.

l	μ	α^0	S = 6			S = 10		
			α_n	α	No. of curve in Fig. 2	α_n	α	No. of curve in Fig. 2
10	0,1	0,01	0,170	0,310	5	0,169	0,309	5
10	0,3	0,01	0,334	0,556	4	0,329	0,550	-
10	0,5	0,01	0,608	0,846	-	0,677	0,887	-
10	0,9	0,01	0,910	0,992	3	1,000	1,000	1
10	0,1	0,1	0,288	0,493	1	0,273	0,472	-
10	0,3	0,1	0,580	0,723	2	0,591	0,832	-
10	0,9	0,1	0,966	0,999	-	0,926	0,995	-
100	0,9	0,1	0,899	0,990	-	0,899	0,989	-
100	0,1	0,01	0,088	0,165	-	0,084	0,161	4
100	0,5	0,01	0,691	0,905	-	0,680	0,898	2
100	0,1	0,001	0,052	0,100	-	0,052	0,101	-
100	0,3	0,001	0,246	0,422	-	0,246	0,431	-
100	0,5	0,001	0,535	0,784	-	0,530	0,779	-
100	0,9	0,001	0,870	0,983	-	0,854	0,979	-
500	0,5	0,01	0,590	0,830	-	0,592	0,837	3
500	0,5	0,001	0,535	0,785	-	0,537	0,786	-

The results of the calculations of the energy and the normal momentum accommodation coefficients for modified initial conditions are shown in Table 2, while the dependence of the velocity of gas atoms with various interaction parameters in the course of collision are shown in Figures 2 and 3.

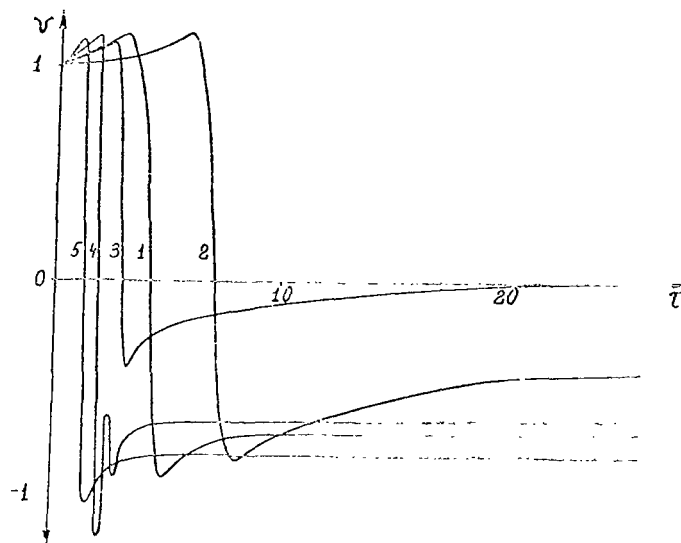


Figure 2. Changes of the velocity of gas atom during collision with linear chain (number of atoms in chain $S = 6$):

1 - $\mu = 0,1$, $l = 10$, $\alpha^0 = 0,1$; 2 - $\mu = 0,3$, $l = 10$, $\alpha^0 = 0,1$; 3 - $\mu = 0,9$, $l = 10$, $\alpha^0 = 0,01$; 4 - $\mu = 0,3$, $l = 10$, $\alpha^0 = 0,01$; 5 - $\mu = 0,1$, $l = 10$, $\alpha^0 = 0,01$

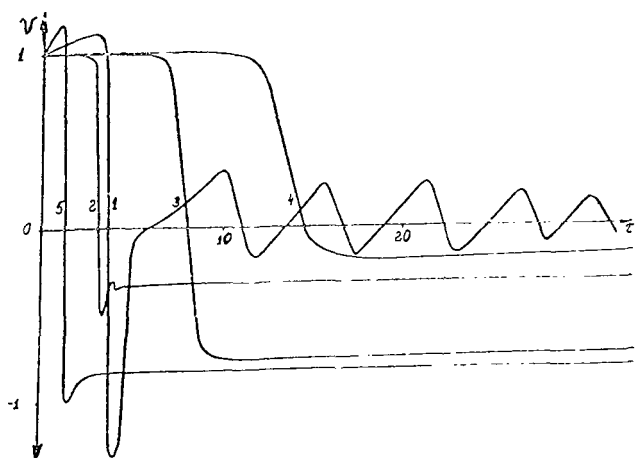


Figure 3. Change in gas atom velocity upon collision with linear chain ($S = 10$):

1 - $\mu = 0,9$, $l = 10$, $\alpha^0 = 0,01$; 2 - $\mu = 0,5$, $l = 100$, $\alpha^0 = 0,01$; 3 - $\mu = 0,5$, $l = 500$, $\alpha^0 = 0,01$; 4 - $\mu = 0,1$, $l = 100$, $\alpha^0 = 0,01$; 5 - $\mu = 0,1$, $l = 10$, $\alpha^0 = 0,01$

5. Numerical solution for the models of interaction
with a three-dimensional crystal. Averaging of
the accommodation coefficients

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In contrast to the one-dimensional model, the three-dimensional model of a solid is more complex when one considers the problem of the interaction between a gas and a surface. This is manifested not only in the fact that mathematically the problem is more difficult, but also in the complexity of the construction of an acceptable model for the crystal and the interaction potentials with close to real properties. Therefore, the purpose of the initial work in this area was to calculate the accommodation coefficients as functions of interaction parameters and to compare them with similar problems in a one-dimensional formulation [11, 12].

Let us consider the case when gas atoms undergo only frontal collisions with the surface atoms, located at the nodes of a cubic lattice. A gas atom interacts either only with the initial atom, or with a whole set of surface atoms, the number of which may be estimated by the methods discussed in Section 2. Let us initially consider the first possibility. The force of interaction of all internal atoms in the block depends on the relative displacement of atoms while the angle of incidence of gas particles upon the wall is random.

The dependence of the accommodation coefficients on the nature of forces which bond the initial atom in the lattice to the neighboring atoms, was investigated in the following variants of this problem:

a) collision of gas atoms with the initial atom, when elastic forces with the constant κ , identical in all directions, are operative between the atoms of the wall from the direction of the closest neighbors;

b) the collision of a gas atom with the initial atom, which is bound to the nearest neighbors by the potential (1), while the bond of the remaining wall atoms is elastic.

The infinite system of equations (5) for both variants does not change its form and the only difference is in the right-hand sides of the equation. In the solution one can devise some scheme similar to the successive approximations scheme, based on the successive evaluation of

the effect exerted on the binary interaction by further and further removed neighbors. The comparison of these "approximations" allows the evaluation of both the qualitative and quantitative effects of neighboring atoms of the corresponding order (with respect to the distance away from the initial lattice atom) on the lattice reaction and consequently, on the magnitude of the accommodation coefficients. /132

The system of equations is reduced to a first-order system of dimensionless form and can be solved numerically. Extensive quantitative data were obtained from which one can draw the following basic qualitative conclusions:

1) in the case of an elastic bond of the initial lattice atom for light particles ($\mu = 0.1$), the energy accommodation coefficient in the case of normal interaction depends very little on the energy of oncoming particles; on the other hand, if the trajectory slopes, the dependence of α on the initial energy will be more clearly expressed; the lesser the slope θ , the greater are the energy losses;

2) in the case of average μ values (~ 0.5), the dependence on θ at high energies is smaller than for the case of average energy;

3) the difference in "approximations" is significant only at low energies, while in the case of average and high energies, the accommodation coefficient values are close (within 5%);

this is possibly a consequence of the postulated lattice isotropy and the increase in its rigidity as a result of the entry of a large number of atoms into motion;

4) the interaction duration in all cases is inversely dependent on the initial energy of the colliding particle and increases somewhat for sloping trajectories in comparison with normal trajectories (by 3%);

5) a significant dependence of energy and momentum exchange on the nature of interatomic forces within the lattice was discovered.

Even within the framework of the head-on collision, the proposed scheme for successive calculations during the interaction of more distant atoms within the lattice allows investigation of the collective nature of interactions. The obtained dependence of velocity of the oncoming

particle on time is very similar to the corresponding dependence for binary collisions. The duration of the interactions is practically unchanged, but the energy losses increase somewhat. For instance, the increase for $\mu = 0.5$ is 18% when $t = 10$, 2.2% when $t = 100$ and 0.8% when $t = 1000$ in comparison with the binary interactions under the same conditions.

Study of frontal collisions gives a qualitative picture of the gas crystal interaction and allows calculation of the accommodation coefficient only for fixed trajectories. Quantitatively more or less reliable values of these coefficients (assuming that the model and interaction parameters are sufficiently close to the real ones) are some average characteristics for all trajectories, which cross an elementary cell at the surface of monocrystal. As before, the collective interaction is manifested in the fact that the collision of an individual gas atom occurs with the whole block of gas atoms.

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One would expect that the transfer of momentum and energy of a gas particle to a crystal in the case of nonfrontal collision will depend on the initial lattice state to a larger extent than in the case of frontal impacts. For example, as a result of thermal oscillation of surface atoms, more precisely, as a result of their displacement from equilibrium positions, the penetration of a gas atom into the crystal can be made easier. Henceforth, it is assumed that the atoms of solids at the initial moment have nonzero velocities and displacements. The assumption that flow around the body occurs as a monoenergetic flow of rarefield gas is quite argumentative for the considered interaction energies; however, one cannot state a priori that the accommodation coefficient is independent of the energy distribution of the oncoming particles. In order to finalize formulation of the problem, it is necessary to take into account the distribution of characteristic velocities in the oncoming stream.

Since it is sufficient to take into account only those gas atoms which in the initial moment interact with an elementary crystal cell, in order to obtain averaged accommodation coefficients, the initial conditions can be tested on some control surface. This surface is subdivided into

cells, the dimensions of which are determined by the magnitude of force of interaction on an individual gas atom from the direction of the block of lattice atoms near the surface target point. The dimensions of the block of atoms of the solid will depend on the required calculation and the computer capabilities. In accordance with the estimates made in Section 2, in the calculation a $3 \times 3 \times 4$ block was used in which each atom interacts only with its nearest neighbor. The writing of the system of equations and initial conditions can now be performed quite readily.

The calculations of the energy tangential momentum and normal momentum accommodation coefficients are conducted on the basis of the trajectories for the case of assigned macrovelocities of the gas atoms of a given mass. /134
The interaction begins ($\tau = 0$) after the passage of gas atoms through the control surface at a relative distance of two from the body surface. The distribution of the projections of target points inside the cell is assumed to be uniform, while the specific target point is defined by the ϑ and Ψ angles. The accommodation coefficients for the trajectory in the case of a fixed initial position of the gas atoms are obtained by averaging the velocities of this atom, which have a distribution in the form of a Maxwellian function

$$f(\vec{u}) = \left(\frac{M}{2\pi kT} \right)^{3/2} \exp \left[- \frac{M(\vec{v} - \vec{u})^2}{2kT} \right].$$

The macrovelocity v , at the initial time is assigned through the l parameters by the formula $\sqrt{l\alpha^0/\mu}$.

The number of trajectories which penetrate a given cell is limited through the use of the ϑ angle and the condition $\tan \vartheta \leq 3/4$, $0 \leq \Psi \leq 2\pi$. After averaging all possible trajectories (or target points) accommodation coefficients are obtained which characterize energy and momentum exchange between the solid and the beam of gas atoms with the stipulated macroscopic velocity.

A change in the parameters μ , α^0 , l , θ , Φ does not change the computation scheme, while a comparison of the numerical values of the obtained

coefficient α , α_T , α_n established the dependence of interaction on these parameters. The average accommodation coefficient values for trajectories are calculated from 125 points, and the number of all possible trajectories in the cell depends on the parameters of the given variant, as many as 50-60.

In calculations, the following values of the parameters were used:
 $\mu = 0.1 - 0.3$; $\alpha^0 = 0.01$; $l = 10 - 100$; $\theta = 0^\circ - 70^\circ$; $\Phi = 0^\circ - 360^\circ$;
 $v = 8 \sqrt{2kT/M}$. Limiting the choice of the Φ values only in the first quadrant can be justified only for not very large values of the θ angle (up to $30^\circ - 35^\circ$). In this case, as control computations have shown, the interaction scheme possesses almost central symmetry. For values $\theta > 35^\circ$, the accommodation coefficients exhibit a strong dependence on the azimuthal angle Φ . Figure 4 shows the dependence of the coefficients α , α_T , α_n on Φ respectively within the limits of one quadrant for a fixed value $\theta = 35^\circ$. Curves 1 and 2 were constructed for the values $\mu = 0.1$, and curves 3 and 4 for the value $\mu = 0.3$. The values of parameter l are also limiting, $l = 10$ for curves 1 and 3, and $l = 100$ for curves 2 and 4. Let us note that the dependence of the accommodation coefficient on the initial energy is not the same different values of the mass ratio μ . For example, while for $\mu = 0.1$ with an increase in the initial energy, the energy accommodation coefficient decreases, for $\mu = 0.3$ the dependence on the orientation of the initial vector \vec{v} and generally for almost all Φ and θ values the coefficient α increases with an increase in the parameter l . The control calculations give similar dependences for $\mu > 0.3$. The coefficients α_T and α_n are more complexly dependent on l and μ , as can be seen in the specific case shown in Figure 4. The decrease in the coefficients α and α_n with an increase in the θ angle is quite sharp; when θ changes from 0° to 70° the decrease in the magnitude of the coefficients is approximately one order of magnitude (Figure 5). However, the computed α , α_T and α_n values for large θ values must be viewed with great caution since with an increase in θ , the computation error also increases.

Thus, the qualitative picture of the calculated changes of energy, tangential momentum and normal momentum accommodation coefficients, taking

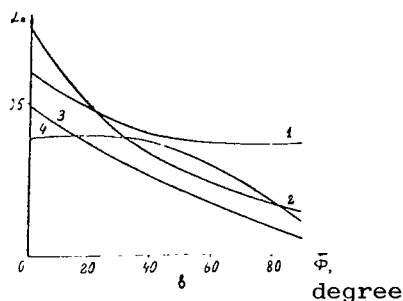
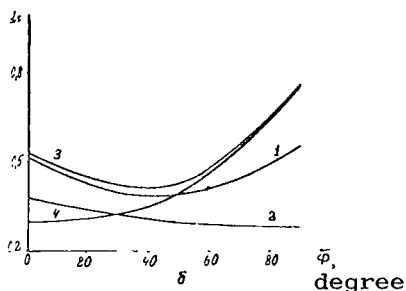
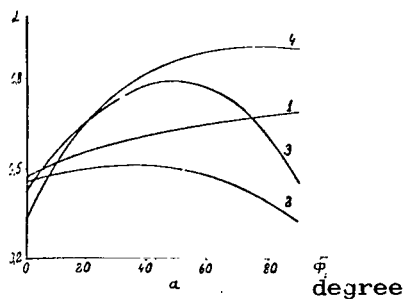


Figure 4. Dependence of accommodation coefficients on the orientation of the initial velocity vector ($\theta = 35^\circ$; $\Phi = 0^\circ - 90^\circ$):

$$\begin{aligned} 1 - \mu = 0, 1, \quad l = 10; \quad 2 - \mu = 0, 1, \quad l = 100; \quad 3 - \mu = 0, 3, \quad l = 10; \quad 4 - \mu = 0, 3, \quad l = 100 \end{aligned}$$

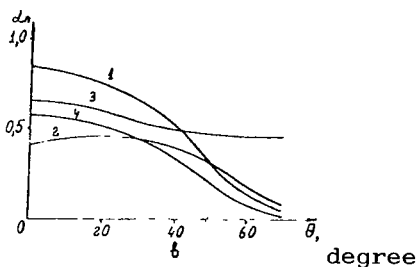
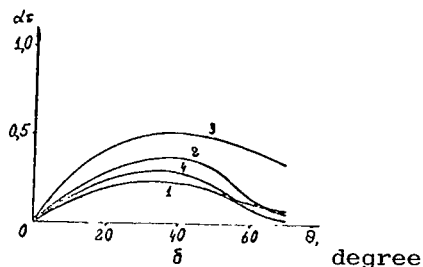
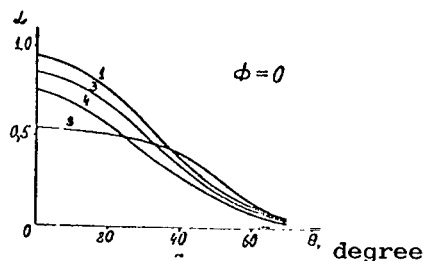


Figure 5. Dependence of the accommodation coefficient on the orientation of the initial velocity vector ($\theta = 0^\circ - 70^\circ$; $\Phi = 0^\circ$):

$$\begin{aligned} 1 - \mu = 0, 1, \quad l = 10; \quad 2 - \mu = 0, 1, \quad l = 100; \quad 3 - \mu = 0, 3, \quad l = 10; \quad 4 - \mu = 0, 3, \quad l = 100 \end{aligned}$$

into account the collective nature of the interaction and averaging for the target points, differs somewhat from the similar picture for a collective interaction, but in the case of an individual trajectory of a gas atom [12]. However, for small θ values, the average accommodation coefficient values even quantitatively are closer to the corresponding values in the case of paired interactions at the same potential than the coefficients obtained in [12]. With the indicated interaction parameters, the average interaction time is practically independent of the selected combination of parameters. In addition, accommodation coefficients calculated for the individual tra-

jectories do not have a large scatter caused by the presence of the characteristic velocity distribution of incident molecules, as one would expect in the case of velocities of the order of the first cosmic velocity. Let us note, however, that with an increase in the θ angle, this dependence becomes significant and apparently for sufficiently large slopes of the incident beam ($\theta \gtrsim 70^\circ$) the accommodation coefficient correction will be comparable to the magnitude of the coefficients themselves.

6. Some Additional Remarks. Possible Improvement in the Accuracy of the Results

The theoretical interaction models which were proposed and considered above /137 are obtained by the varying following principal properties of solids: 1) dimensionality of the block of wall atoms; 2) dimensions of this block; 3) initial state and the form of interatomic bond within the lattice and also the properties of the gas molecules: 1) form of the velocity distribution function; 2) possibility of nonfrontal collisions; 3) type of the interaction potential between gas and solid atoms. In comparing the various models it appears at first glance that the one-dimensional interaction models are weaker than others, at least until there are sufficient experimental data which would enable some rehabilitation of these models. However, despite the artificial nature of the one-dimensional interaction model, a comparison of the calculation results with three-dimensional models shows that the principal qualitative dependence of the energy and momentum exchange coefficients on the initial state, the type of the interatomic bonds within the lattice of the solid and the type of the interaction potential between gas atoms and the wall for these models are very close. The advantage of the one-dimensional problem is the simplicity of formulation and calculation. It is understood that everything said above refers to frontal collisions normal to the collision surface. Therefore, in those problems where various angles of incidence of the gas molecules are considered and nonfrontal collisions are allowed, it is necessary to take into account the three-dimensional nature of the crystal with which the interaction takes place.

A study of individual trajectories is sufficient for determining the qualitative picture of the interaction, however, it is the quantitative results which can be obtained by averaging such parameters as target points and characteristic velocities of gas particles which are of interest. The first of these parameters for the accommodation coefficient was averaged in [13]. A block of atoms of solid was considered which contained 59 atoms, with normal crystal structure of various bodies and it was assumed that the thermal oscillations of lattice atoms can be neglected. The dependence of the averaged energy accommodation coefficient α on the energy of the incident particles ϵ , on the form of the potential of interaction, and also in a special case on the angle of incidence θ at values up to 45° was obtained. The calculation scheme presented in Section 5 for three-dimensional problems allows somewhat larger value of the θ angle, and also the possibility of taking into account the characteristic velocity distribution for gas molecules, so that the computation of the averaged values of the accommodation coefficients no longer presents any great difficulties, regardless of the choice of the interaction parameters (including the type of the potential and the crystal lattice). Only for the large angles of incidence should the above-presented calculation scheme be somewhat altered in form. /138

Considering the large volume of calculations which must be performed for each set of parameters, and also the strong dependence of the coefficients α , α_T , α_n on the target points in comparison with the dependence on the characteristic velocities of gas atoms, it appears feasible to average the characteristic velocities only for large θ angles. The complete qualitative (and also quantitative) picture of the interaction in describing the phenomenon at the level of accommodation coefficients may be determined only after detailed calculations by the above-indicated scheme for the most complete possible selection of the interaction parameters, followed by subsequent comparison of the results with the experimental data; this is feasible using modern computers.

In the above-considered methods for modeling the interaction of a rarefied gas and a solid surface, it was assumed that the surface is clean, i.e., there are no adsorbed atoms. It is true, however, in the Section 5 a possible variant of the interaction was considered in which the bond of the terminal

atom with its neighbors is formed by the same potential as the interaction of a gas atom and wall atoms. Assuming that the mass ratio of gas atoms and the initial atoms (M/m_0) is equal to unity, it is possible to simulate to some extent the interaction with the adsorbed atoms (or even with minor modifications of the scheme, with the adsorbed layer). However, this scheme is too idealized, since the real structure and the forces of interaction with the adsorbed layer are not taken into account. Apparently, in addition to improvement in the scheme of interaction with the adsorption layer, it is necessary to determine the interaction potentials more accurately, which until now were selected for theoretical models either intuitively, making mathematical convenience one of the primary criteria, or based on nonrigorous foundations.

The second assumption which was made for the interaction models, is that surface roughness is absent. In the literature there are a number of works devoted to taking surface roughness into account in interaction problems; however, in these works the attempt is made to either construct a rough surface, or the interaction with this rough surface is considered with stipulated values of the accommodation coefficients. This complex problem still is unsolved. /139
Let us note that taking the surface roughness into account in the theoretical computations of momentum and energy exchange coefficients is the most important refinement in the problem of interaction of a rarefied gas with the surface of streamlined bodies. However, the final choice of theoretical models can be made only when the possibility of testing at least some of the assumptions will become possible in a reliable experiment.

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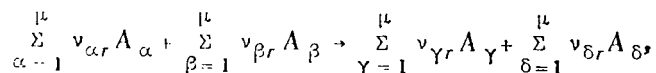
B. V. Alekseyev

The theory of transfer phenomena in nonreacting gas mixtures whose molecules can be viewed as point force centers has already been developed in great detail [1, 2]. The transfer coefficients in the reaction media may be obtained from the ordinary formulae of the rigorous kinetic theory of gases when $e^{\tilde{\epsilon}^*/kT} \gg 1$, where $\tilde{\epsilon}^*$ is the chemical reaction activation energy. However, at elevated temperatures or with sufficiently low activation energies, the number of molecular collisions which lead to chemical reactions may reach the same order of magnitude as the number of the elastic collisions. In this case, the formulae for calculating transfer coefficients in nonreacting gas mixtures does not apply. In this work we consider transfer phenomena in the reacting media. The notation used has been selected to correspond as much as possible to the system of notation used in book [2]. All new designations and those which differ from the notation in book [2] will be identified in the text.

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1. Dynamics of Paired Collisions

In a mixture of gases consisting of μ components, let a number l of bimolecular homogeneous reactions of the following form take place:



where $v_{\alpha r}$, $v_{\beta r}$, $v_{\gamma r}$, $v_{\delta r}$ are stoichiometric coefficients which can be either zero or one. Components A_{α} , A_{β} , A_{γ} , A_{δ} , which possess identical chemical characteristics (and consequently identical molecular weights), are considered different if they have different internal energies ϵ_{α} , ϵ_{β} , ϵ_{γ} , ϵ_{δ} . Molecular collisions in which no mass or internal energy exchanges take place are called elastic; all other collisions are

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inelastic. Let us consider an inelastic collision, the result of which is a chemical reaction:



Nuclear reactions are not considered here; therefore, the law of conservation of mass holds:

$$m_{\alpha} + m_{\beta} = m_{\gamma} + m_{\delta}. \quad (2)$$

The law for conservation of momentum is as follows:

$$m_{\alpha} \vec{v}_{\alpha} + m_{\beta} \vec{v}_{\beta} = m_{\gamma} \vec{v}_{\gamma}' + m_{\delta} \vec{v}_{\delta}' = (m_{\alpha} + m_{\beta}) \vec{G} = (m_{\gamma} + m_{\delta}) \vec{G}, \quad (3)$$

where \vec{G} is the center of mass velocity of the motion, and prime designates the characteristic quantities after the collision. Utilizing equation (3), one can easily obtain the following relationship:

$$\begin{aligned} \vec{v}_{\alpha} &= \vec{G} + M_{\beta} \vec{g}_{\alpha\beta}; & \vec{v}_{\beta} &= \vec{G} + M_{\alpha} \vec{g}_{\beta\alpha}; \\ \vec{v}_{\gamma}' &= \vec{G} + M_{\delta} \vec{g}_{\gamma\delta}'; & \vec{v}_{\delta}' &= \vec{G} + M_{\gamma} \vec{g}_{\delta\gamma}', \end{aligned}$$

where $g_{\beta\alpha}$, for example, is the initial velocity of molecule β relative to the velocity of molecule α . The law of conservation of energy is as follows:

$$\varepsilon_{\alpha} + \varepsilon_{\beta} + \frac{1}{2} m_{\alpha} v_{\alpha}^2 + \frac{1}{2} m_{\beta} v_{\beta}^2 = \varepsilon_{\gamma} + \varepsilon_{\delta} + \frac{1}{2} m_{\gamma} v_{\gamma}'^2 + \frac{1}{2} m_{\delta} v_{\delta}'^2. \quad (4)$$

Consider the law of conservation of energy (4) in the form:

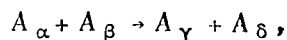
$$\eta - \eta' = \varepsilon_{\gamma} + \varepsilon_{\delta} - \varepsilon_{\alpha} - \varepsilon_{\beta}, \quad (5)$$

where

$$\eta = \frac{m_{\alpha} m_{\beta}}{2(m_{\alpha} + m_{\beta})} g_{\alpha\beta}^2; \quad \eta' = \frac{m_{\gamma} m_{\delta}}{2(m_{\gamma} + m_{\delta})} g_{\gamma\delta}'^2$$

are the kinetic energies of the relative motion of molecules prior to and after the collision, respectively. It follows from equation (5) for the endothermal reaction ($\varepsilon_{\gamma} + \varepsilon_{\delta} > \varepsilon_{\alpha} + \varepsilon_{\beta}$) that the kinetic energy

of the relative motion of the molecules $\eta \geq \epsilon_Y + \epsilon_\delta - \epsilon_\alpha - \epsilon_\beta > 0$; in the case of exothermic reactions, there is no such limitation on the initial kinetic energy with respect to the motion of molecules. Let us designate by $d\omega \overset{r}{P}_{\alpha\beta}^{\gamma\delta}(g_{\alpha\beta}, 0, \varphi, \theta)$ (is the position in the x_2x_3 plane) the probability that a molecule of type β , after collision with a molecule of type α , will fall within the solid angle $\omega, d\omega$; the following reaction will take place:



which will be designated as r (Figure 1).

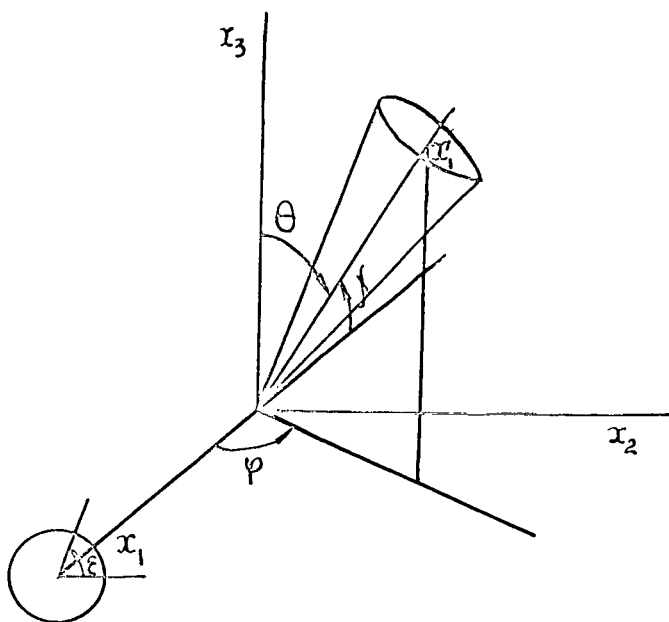


Figure 1: Coordinates which are used in considering inelastic collisions of molecules.

Assume that, upon collision, the principle of macroscopic reversibility takes place if the probability distribution densities $\overset{r}{P}_{\alpha\beta}^{\gamma\delta}, \overset{r}{P}_{\gamma\delta}^{\alpha\beta}$ for the direct and reverse collisions are related by the equation:

$$g_{\alpha\beta} \overset{r}{P}_{\alpha\beta}^{\gamma\delta} b \sin \theta d\theta d\varphi db d\epsilon d\vec{v}_\alpha d\vec{v}_\beta =$$

$$= g_{\gamma\delta} \overset{r}{P}_{\gamma\delta}^{\alpha\beta} b' \sin \theta' d\theta' d\varphi' db' d\epsilon' d\vec{v}_\gamma d\vec{v}_\delta.$$

Appropriate choice of a coordinate system always makes it possible to achieve the following relationship:

$$d\omega = d\omega',$$

and, consequently, the principle of macroscopic reversibility can be reduced to the form:

$$g_{\alpha\beta}^r P_{\alpha\beta}^{\gamma\delta} b db d\varepsilon d\vec{v}_\alpha d\vec{v}_\beta = g_{\gamma\delta}^r P_{\gamma\delta}^{\alpha\beta} b' db' d\varepsilon' d\vec{v}_\gamma d\vec{v}_\delta.$$

Remark 1: As a result of collisions of classical structureless point particles of types α and β (with masses m_α and m_β), let reaction (1) take place, forming particles of types γ and δ (with masses m_γ and m_δ). Then, on the basis of the law of conservation of momentum, it follows that the whole collision process proceeds in one plane, and the impact parameters before and after collisions are related by the formula:

$$m_\alpha m_\beta b g_{\alpha\beta} = m_\gamma m_\delta b' g_{\gamma\delta}.$$

If the collision of particles takes place in one plane, then geometric parameters ε and ε' may be selected equal. It is possible to show that in this case the following formula holds:

$$\left(\frac{m_\gamma m_\delta}{m_\alpha m_\beta}\right)^3 P_{\alpha\beta}^{\gamma\delta} = P_{\gamma\delta}^{\alpha\beta}. \quad (5')$$

However, it is well known that the bimolecular reaction is a complex reaction which involves the formation of quasimolecules (activated complex). Apparently, during the destruction of quasimolecules, the particles which are formed do not scatter in the same plane in which the collision took place. Formula (5') is therefore of little use. At present, the values of the probability $P_{\alpha\beta}^{\gamma\delta}$ for chemical reactions cannot be expressed as a function of angles θ and φ . Therefore, in calculating the collision integrals, we shall hypothesize isotropic scattering. Specifically, we shall assume that

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during the destruction of quasimolecules, all scattering directions for the escaping particles are equiprobable.

2. Enskog Method for Solving the Boltzmann Equation, Taking into Account Inelastic Collisions

The Boltzmann equation may be written in the form

$$\frac{\partial f_\alpha}{\partial t} + \vec{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{r}} + \vec{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{v}_\alpha} = \left(\frac{\partial_e f_\alpha}{\partial t} \right)_{el} + \left(\frac{\partial_e f_\alpha}{\partial t} \right)_r,$$

where

$$\left(\frac{\partial_e f_\alpha}{\partial t} \right)_{el} = \sum_{j=1}^{\mu} \iiint (f'_\alpha f'_j - f_\alpha f_j) g_{\alpha j} P_{\alpha j}^{\alpha j} b db d\epsilon d\vec{v}_j;$$

$$\left(\frac{\partial_e f_\alpha}{\partial t} \right)_r = \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \iiint (f'_\gamma f'_\delta - f_\gamma f_\delta) g_{\alpha \beta} P_{\alpha \beta}^{\gamma \delta} \sin \theta b db d\epsilon d\vec{v}_\beta.$$

Let us consider a hypothetical problem for which the two collision terms on the right side of the Boltzmann equation have the form

$$\frac{\partial f_\alpha}{\partial t} + \vec{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{r}} + \vec{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{v}_\alpha} = \frac{1}{\epsilon} \left(\frac{\partial_e f_\alpha}{\partial t} \right)_{el} + \frac{1}{\delta} \left(\frac{\partial_e f_\alpha}{\partial t} \right)_r,$$

where $1/\epsilon$ and $1/\delta$ are measures of the frequency of elastic and inelastic collisions, respectively. When $1/\delta \ll 1/\epsilon$, the collisions resulting in chemical reactions are much less frequent than elastic collisions. It is possible to show that an additional scalar term appears in the first approximation of the general solution of integro-differential Boltzmann equations. Excitation and initiation reactions within the framework of this approximation were investigated in references [3, 4]. We shall consider another limiting case ($1/\delta \sim 1/\epsilon$), which takes place, for instance, at elevated temperatures when $\tilde{\epsilon} \approx kT$ ($\tilde{\epsilon}^*$ is the activation energy of the chemical reaction).

Let us represent a distribution function f_α in the form

$$f_\alpha = \sum_{k=0}^{\infty} \epsilon^k f_\alpha^{(k)} \quad (\alpha = 1, \dots, \mu).$$

For the distribution function $f_\alpha^{(0)}$ we obtain the equation:

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$$0 = \left(\frac{\partial f_{\alpha}^{(0)}}{\partial t} \right)_{el} + \left(\frac{\partial f_{\alpha}^{(0)}}{\partial t} \right)_r \quad (6)$$

From equation (6) we obtain a Maxwellian distribution function for the system in equilibrium:

$$f_{\alpha}^{(0)} = n_{\alpha} \left(\frac{m_{\alpha}}{2\pi kT} \right)^{3/2} e^{-\frac{m_{\alpha} V_{\alpha}^2}{2kT}}. \quad (7)$$

The Maxwellian distribution (7) corresponds to the following system of summation invariants:

$$m_{\alpha}, m_{\alpha} \vec{V}_{\alpha}, \frac{m_{\alpha} V_{\alpha}^2}{2} + \varepsilon_{\alpha}.$$

Remark 2: For the summation invariant $n_{\tau\alpha}$ ($n_{\tau\alpha}$ is the number of atoms of type τ in a molecule of α components, where $\alpha = 1, \dots, \mu$), from the hydrodynamic Enskog equations one can obtain ν diffusion equations for a chemical element [5]. However, these equations will not be new and independent, since they result from μ diffusion equations for the components. Therefore, $n_{\tau\alpha}$ is not used as a new independent invariant.

In the first approximation the Boltzmann equation has the form:

$$\begin{aligned} \frac{\partial f_{\alpha}^{(0)}}{\partial t} + \vec{v}_{\alpha} \cdot \frac{\partial f_{\alpha}^{(0)}}{\partial \vec{r}} + \vec{F}_{\alpha} \cdot \frac{\partial f_{\alpha}^{(0)}}{\partial \vec{v}_{\alpha}} = & \sum_{j=1}^{\mu} \iiint f_{\alpha}^{(0)} f_j^{(0)} (\Phi_{\alpha} + \Phi_j' - \Phi_{\alpha} - \\ & - \Phi_j) g_{\alpha j} P_{\alpha j}^{\alpha j} b db d\varepsilon d\vec{v}_j + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \iiint f_{\alpha}^{(0)} f_j^{(0)} (\Phi_{\alpha}' + \Phi_{\delta}' - \Phi_{\alpha} - \\ & - \Phi_{\beta}) g_{\alpha \beta} P_{\alpha \beta}^{\gamma \delta} \sin \theta b db d\theta d\varepsilon d\varphi d\vec{v}_{\beta}, \quad (\alpha = 1, \dots, \mu). \end{aligned} \quad (8)$$

An additional condition is written in an ordinary fashion:

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$$\int f_{\alpha}^{(0)} \Phi_{\alpha} d\vec{v}_{\alpha} = 0;$$

$$\sum_{\alpha} m_{\alpha} \int \vec{v}_{\alpha} f_{\alpha}^{(0)} \Phi_{\alpha} d\vec{v}_{\alpha} = 0;$$

$$\sum_{\alpha} m_{\alpha} \int (\vec{v}_{\alpha} - \vec{v}_0)^2 f_{\alpha}^{(0)} \Phi_{\alpha} d\vec{v}_{\alpha} = 0.$$

The operator

$$D_{\alpha} f = \frac{\partial f_{\alpha}}{\partial t} + \vec{v}_{\alpha} \cdot \frac{\partial f_{\alpha}}{\partial \vec{r}} + \vec{F}_{\alpha} \cdot \frac{\partial f_{\alpha}}{\partial \vec{v}_{\alpha}}$$

for the distribution function $f_{\alpha}^{(0)}$ has the form

$$D_{\alpha}^{(0)} f = f_{\alpha}^{(0)} \left\{ \frac{K_{\alpha}^{(0)}}{n_{\alpha}} + \frac{1}{p} \left(1 - \frac{2}{3} W_{\alpha}^2 \right) \sum_i m_i K_i^{(0)} \hat{U}_i + \vec{V}_{\alpha} \cdot \left(W_{\alpha}^2 - \frac{5}{2} \right) \frac{d \ln T}{d \vec{r}} + \frac{n}{n_{\alpha}} \vec{V}_{\alpha} \cdot \vec{d}_{\alpha} + 2 \vec{W}_{\alpha}^0 \vec{W}_{\alpha} : \frac{\partial}{\partial \vec{r}} \vec{v}_0 \right\},$$

where $\vec{W}_{\alpha}^0 \vec{W}_{\alpha}$ is a nondivergent tensor $\vec{W}_{\alpha}^0 \vec{W}_{\alpha} = \frac{1}{3} W_{\alpha}^2 U$; K_{α} is the number of type α particles formed per unit volume per unit time at the expense of all homogeneous reactions

$$K_{\alpha} = \int \left(\frac{\partial f_{\alpha}}{\partial t} \right)_r d\vec{v}_{\alpha},$$

\hat{U}_i is the thermodynamic internal energy per gram: $\hat{U}_i = \overline{V_i^2}/2 + \varepsilon_i/m_i$.

In this case $K_{\alpha}^{(0)} = 0$ and the operator $D_{\alpha}^{(0)}$ has an ordinary form:

$$D_{\alpha}^{(0)} = f_{\alpha}^{(0)} \left\{ \vec{V}_{\alpha} \cdot \left(W_{\alpha}^2 - \frac{5}{2} \right) \frac{d \ln T}{d \vec{r}} + \frac{n}{n_{\alpha}} \vec{V}_{\alpha} \cdot \vec{d}_{\alpha} + 2 \vec{W}_{\alpha}^0 \vec{W}_{\alpha} : \frac{\partial}{\partial \vec{r}} \vec{v}_0 \right\},$$

where

$$\vec{d}_{\alpha} = \frac{\partial}{\partial \vec{r}} \left(\frac{n}{n_{\alpha}} \right) + \left(\frac{n_{\alpha}}{n} - \frac{\rho_{\alpha}}{\rho} \right) \frac{\partial \ln p}{\partial \vec{r}} - \frac{\rho_{\alpha}}{p \rho} \left[\rho \vec{F}_{\alpha} - \sum_{j=1}^{\mu} \rho_j \vec{F}_j \right].$$

The general solution of the system of linear integral equations (8) may be found in the form

$$\Phi_{\alpha} = - \left(\vec{\Lambda} \cdot \frac{\partial \ln T}{\partial \vec{r}} \right) - B_{\alpha} : \frac{\partial}{\partial \vec{r}} \vec{v}_0 + n \sum_{j=1}^{\mu} \vec{C}_{\alpha}^{(j)} \cdot \vec{d}_j. \quad (9)$$

Substituting Φ_{α} from (9) into equation (8) and equating the coefficients, we obtain a system of integral equations linear with respect to functions A_{α} , B_{α} , $\vec{C}_{\alpha}^{(j)}$:

$$f_{\alpha}^{(0)} \left(\frac{5}{2} - W_{\alpha}^2 \right) \vec{V}_{\alpha} = \sum_{j=1}^{\mu} \iiint (\vec{A}'_{\alpha} + \vec{A}'_j - \Lambda_{\alpha} -$$

$$\begin{aligned}
& -A_j)P_{\alpha j}^{\alpha j} f_{\alpha}^{(0)} f_j^{(0)} g_{\alpha j} bdbd\varepsilon d\vec{v}_j + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \iiiii (\vec{A}'_{\gamma} + \vec{A}'_{\delta} - \\
& -A_{\alpha} - A_{\beta}) f_{\alpha}^{(0)} f_{\beta}^{(0)} g_{\alpha \beta} P_{\alpha \beta}^{\gamma \delta} \sin \theta bdbd\theta d\varepsilon d\varphi d\vec{v}_{\beta}; \quad (10)
\end{aligned}$$

$$\begin{aligned}
2f_{\alpha}^{(0)} \vec{W}_{\alpha}^0 \vec{W}_{\alpha} = & -\sum_{j=1}^{\mu} \iiiii (B'_{\alpha} + B'_j - B_{\alpha} - B_j) f_{\alpha}^{(0)} f_j^{(0)} P_{\alpha j}^{\alpha j} g_{\alpha j} \times \\
& \times bdbd\varepsilon d\vec{v}_j + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \iiiii (B'_{\gamma} + B'_{\delta} - B_{\alpha} - \\
& - B_{\beta}) f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha \beta}^{\gamma \delta} \sin \theta bdbd\theta d\varepsilon d\varphi d\vec{v}_{\beta}; \quad (11)
\end{aligned}$$

$$\begin{aligned}
\frac{1}{n_{\alpha}} f_{\alpha}^{(0)} \vec{V}_{\alpha} (\delta_{\alpha h} - \delta_{\alpha k}) = & \sum_{j=1}^{\mu} \iiiii (\vec{C}_{\alpha}^{(h)'} + \vec{C}_j^{(h)'} - \vec{C}_{\alpha}^{(k)'} - \vec{C}_j^{(k)'} - \\
& - \vec{C}_{\alpha}^{(h)} - \vec{C}_j^{(h)} + \vec{C}_{\alpha}^{(k)} + \vec{C}_j^{(k)}) f_{\alpha}^{(0)} f_j^{(0)} P_{\alpha j}^{\alpha j} g_{\alpha j} bdbd\varepsilon d\vec{v}_j + \\
& + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \iiiii (\vec{C}_{\gamma}^{(h)'} + \vec{C}_{\delta}^{(h)'} - \vec{C}_{\gamma}^{(k)'} - \vec{C}_{\delta}^{(k)'} - \vec{C}_{\alpha}^{(h)} - \vec{C}_{\beta}^{(h)} + \\
& + \vec{C}_{\alpha}^{(k)} + \vec{C}_{\beta}^{(k)}) f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha \beta}^{\gamma \delta} g_{\alpha \beta} \sin \theta bdbd\varepsilon d\varphi d\theta d\vec{v}_{\beta}. \quad (12)
\end{aligned}$$

One can easily determine that the following conditions for the solution of linear integral equations (10), (11), and (12) are fulfilled:

$$\begin{aligned}
\sum_{\alpha} \int f_{\alpha}^{(0)} \left(\frac{5}{2} - W_{\alpha}^2 \right) \vec{V}_{\alpha} \psi_{\alpha} d\vec{V}_{\alpha} &= 0; \\
\sum_{\alpha} \int f_{\alpha}^{(0)} \vec{W}_{\alpha}^0 \vec{W}_{\alpha} \psi_{\alpha} d\vec{V}_{\alpha} &= 0; \\
\sum_{\alpha} \frac{1}{n_{\alpha}} (\delta_{\alpha h} - \delta_{\alpha k}) \int f_{\alpha}^{(0)} \vec{V}_{\alpha} \psi_{\alpha} d\vec{V}_{\alpha} &= 0.
\end{aligned}$$

Integral equations (10)-(12) may be written in general form as follows:

$$\begin{aligned}
R_{\alpha}^{(hk)} = & \sum_j \iiiii (T_{\alpha}^{(hk)'} + T_j^{(hk)'} - T_{\alpha}^{(hk)} - T_j^{(hk)}) f_{\alpha}^{(0)} f_j^{(0)} \times \\
& \times P_{\alpha j}^{\alpha j} g_{\alpha j} bdbd\varepsilon d\vec{v}_j + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \iiiii (T_{\gamma}^{(hk)'} + T_{\delta}^{(hk)'} - \\
& - T_{\alpha}^{(hk)} - T_{\beta}^{(hk)}) f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha \beta}^{\gamma \delta} g_{\alpha \beta} \sin \theta bdbd\theta d\varepsilon d\varphi d\vec{v}_{\beta}; \quad (13)
\end{aligned}$$

Equation Number	$R_{\alpha}^{(hk)}$	$T_{\alpha}^{(hk)}$
(10)	$f_{\alpha}^{(0)} \left(\frac{5}{2} - W_{\alpha}^2 \right) \vec{V}_{\alpha}$	\vec{A}_{α}
(11)	$\frac{1}{n_{\alpha}} f_{\alpha}^{(0)} \vec{V}_{\alpha} (\delta_{\alpha h} - \delta_{\alpha k})$	$\vec{C}_{\alpha}^{(h)} - \vec{C}_{\alpha}^{(k)}$
(12)	$-2 f_{\alpha}^{(0)} \vec{W}_{\alpha}^0 \vec{W}_{\alpha}$	B_{α}

Additional conditions for equations (10) and (11) are as follows:

$$\sum_{\alpha} \sqrt{m_{\alpha}} \int (T_{\alpha}^{(hk)} \cdot \vec{W}_{\alpha}) f_{\alpha}^{(0)} d\vec{v}_{\alpha} = 0.$$

There is no additional condition for equation (12).

3. Variation Principle

Before using the variation principle to find an approximate solution of integral equation (13), let us prove several integral theorems.

Consider the expression

$$J = \sum_r \sum_{\alpha\beta\gamma\delta} \iiint K_{\alpha} : [K'_{\gamma} + K'_{\delta} - K_{\alpha} - K_{\beta}] \times f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} \sin \theta b d\theta d b d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta},$$

where K_{α} , for example, is a tensor function dependent on \vec{W}_{α} . Indices r, α, β, γ , and δ are mute. Replace index α with γ and index β with δ . We then obtain

$$J = \sum_r \sum_{\alpha\beta\gamma\delta} \iiint K_{\gamma} : [K'_{\alpha} + K'_{\beta} - K_{\gamma} - K_{\delta}] \times \times f_{\gamma}^{(0)} f_{\delta}^{(0)} P_{\gamma\delta}^{\alpha\beta} g_{\gamma\delta} \sin \theta b d\theta d b d\epsilon d\varphi d\vec{v}_{\gamma} d\vec{v}_{\delta}. \quad (14) \quad \underline{149}$$

Utilizing the principle of microscopic reversibility in the form

$$P_{\gamma\delta}^{\alpha\beta} g_{\gamma\delta} \sin \theta b d\theta d b d\epsilon d\varphi d\vec{v}_{\gamma} d\vec{v}_{\delta} = P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} \sin \theta' b' d\theta' d b' d\epsilon' d\varphi' d\vec{v}_{\alpha}' d\vec{v}_{\beta}' \quad (15)$$

and the relationship

$$f_{\alpha}^{(0)} f_{\beta}^{(0)} = f_{\gamma}^{(0)} f_{\delta}^{(0)}. \quad (16)$$

Substituting (15) and (16) into formula (14) and considering collisions $\gamma + \delta$ reversible, we find

$$J = \sum_r \sum_{\alpha\beta\gamma\delta} \iiint K'_{\gamma} : [K_{\alpha} + K_{\beta} - K'_{\gamma} - K'_{\delta}] \times \\ \times f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta}.$$

Thus, the following formula has been proved:

$$\sum_r \sum_{\alpha\beta\gamma\delta} \iiint K_{\alpha} : [K'_{\gamma} + K'_{\delta} - K_{\alpha} - K_{\beta}] f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta \times \\ \times db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta} = - \sum_r \sum_{\alpha\beta\gamma\delta} \iiint K'_{\gamma} : [K'_{\gamma} + K'_{\delta} - K_{\alpha} - \\ - K_{\beta}] f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta}.$$

Substituting α for β , the following formula can be obtained

$$\sum_r \sum_{\alpha\beta\gamma\delta} \iiint K_{\alpha} : [K'_{\gamma} + K'_{\delta} - K_{\alpha} - K_{\beta}] f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db \times \\ \times d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta} = \sum_r \sum_{\alpha\beta\gamma\delta} \iiint K_{\beta} : [K'_{\gamma} + K'_{\delta} - K'_{\alpha} - \\ - K_{\beta}] f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta}. \quad (17)$$

Replacing α by β and γ by δ and utilizing relationship (17), we obtain /150

$$\sum_r \sum_{\alpha\beta\gamma\delta} \iiint K_{\alpha} : [K'_{\gamma} + K'_{\delta} - K_{\alpha} - K_{\beta}] f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db \times \\ \times d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta} = - \sum_r \sum_{\alpha\beta\gamma\delta} \iiint K'_{\delta} : [K'_{\gamma} + K'_{\delta} - K_{\alpha} - \\ - K_{\beta}] f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta}.$$

Let $\{K, K\}^r$ be the operator

$$\{K, K\}^r = - \sum_r \sum_{\alpha\beta\gamma\delta} \iiint (K_{\alpha} + K_{\beta}) : (K'_{\gamma} + K'_{\delta} - K_{\alpha} - K_{\beta}) \times \\ \times f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta},$$

then $\{K, K\}^r = -\frac{1}{2} \sum_r \sum_{\alpha\beta\gamma\delta} \int \int \int \int K_\alpha : (K'_\gamma + K'_\delta - K_\alpha - K_\beta) \times$
 $\times f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^r g_{\alpha\beta} b \sin \theta b d \theta d \varepsilon d \varphi d \vec{v}_\alpha d \vec{v}_\beta.$

Consequently, $\{K, K\}^r = \frac{1}{2} \sum_r \sum_{\alpha\beta\gamma\delta} \int \int \int \int [K'_\gamma + K'_\delta - K_\alpha - K_\beta] : [K'_\gamma + K'_\delta -$
 $- K_\alpha - K_\beta] f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^r g_{\alpha\beta} b \sin \theta b d \theta d \varepsilon d \varphi d \vec{v}_\alpha d \vec{v}_\beta.$

Since the possible form of the tensors K_α , K_β , K_δ , and K_γ is a dyad, then

$$\{K, K\}^r \geq 0. \quad (18)$$

Analogously, if $\{K, L\}^r$ is an operator

$$\{K, L\}^r = -\sum_r \sum_{\alpha\beta\gamma\delta} \int \int \int \int (K_\alpha + K_\beta) : (L'_\gamma + L'_\delta - L_\alpha - L_\beta) \times$$

$$\times f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^r g_{\alpha\beta} b \sin \theta b d \theta d \varepsilon d \varphi d \vec{v}_\alpha d \vec{v}_\beta,$$

then

$$\{K, L\}^r = \frac{1}{2} \sum_r \sum_{\alpha\beta\gamma\delta} \int \int \int \int (K'_\gamma + K'_\delta - K_\alpha - K_\beta) : (L'_\gamma + L'_\delta - L_\alpha -$$

$$- L_\beta) f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^r g_{\alpha\beta} b \sin \theta b d \theta d \varepsilon d \varphi d \vec{v}_\alpha d \vec{v}_\beta. \quad (19)$$

From relationship (19) it follows that

$$\{K, L\}^r = \{L, K\}^r.$$

Let us now assume that we have a tensor function $t_\alpha^{(hk)}$ which satisfies the equations:

$$\int (t_\alpha^{(hk)} : R_\alpha^{(hk)}) d\vec{v}_\alpha = \sum_j \int \int \int t_\alpha^{(hk)} : (t_\alpha^{(hk)} + t_j^{(hk)} -$$

$$- t_\alpha^{(hk)} - t_j^{(hk)}) g_{\alpha j} P_{\alpha j}^{\alpha j} b d b d \varepsilon d \vec{v}_\alpha d \vec{v}_j + \frac{1}{2} \sum_r \sum_{\beta\gamma\delta} \int \int \int \int t_\alpha^{(hk)} :$$

$$: (t_\gamma^{(hk)} + t_\delta^{(hk)} - t_\alpha^{(hk)} - t_\beta^{(hk)}) f_\alpha^{(0)} f_\beta^{(0)} P_{\alpha\beta}^r g_{\alpha\beta} b \sin \theta \times$$

$$\times b d b d \theta d \varepsilon d \varphi d \vec{v}_\alpha d \vec{v}_\beta.$$

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Let us biscalarly multiply integral equations (13) by the trial tensor functions $t_{\alpha}^{(hk)}$, and integrate the obtained binary tensor product over all values of \vec{v}_{α} . Then, equating the right-hand sides of the obtained equation to the right-hand sides of equations (21), we can sum for all of α ($\alpha = 1, \dots, \mu$). If one also takes relationship (17) into account, we obtain

$$\begin{aligned} & \sum_{\alpha j} \iiint (t_{\alpha}^{(hk)} + t_j^{(hk)}) : (t_{\alpha}^{(hk)} + t_j^{(hk)} - t_{\alpha}^{(hk)} - t_j^{(hk)}) f_{\alpha}^{(0)} f_j^{(0)} P_{\alpha j}^{\alpha j} g_{\alpha j} b db d\epsilon d\vec{v}_{\alpha} d\vec{v}_j + \\ & + \frac{1}{2} \sum_{r=1}^l \sum_{\alpha \beta \gamma \delta} \iiint (t_{\alpha}^{(hk)} + t_{\beta}^{(hk)}) : (t_{\gamma}^{(hk)} + t_{\delta}^{(hk)} - \\ & - t_{\alpha}^{(hk)} - t_{\beta}^{(hk)}) f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha \beta}^{\alpha \beta} g_{\alpha \beta} b \sin \theta db d\epsilon d\vec{v}_{\alpha} d\vec{v}_{\beta} = \\ & = \sum_{\alpha j} \iiint (t_{\alpha}^{(hk)} + t_j^{(hk)}) : (T_{\alpha}^{(hk)} + T_j^{(hk)} - T_{\alpha}^{(hk)} - \\ & - T_j^{(hk)}) f_{\alpha}^{(0)} f_j^{(0)} P_{\alpha j}^{\alpha j} g_{\alpha j} b db d\epsilon d\vec{v}_{\alpha} d\vec{v}_j + \\ & + \frac{1}{2} \sum_{r=1}^l \sum_{\alpha \beta \gamma \delta} \iiint (t_{\alpha}^{(hk)} + t_{\beta}^{(hk)}) : (T_{\gamma}^{(hk)} + T_{\delta}^{(hk)} - \\ & - T_{\alpha}^{(hk)} - T_{\beta}^{(hk)}) f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha \beta}^{\alpha \beta} g_{\alpha \beta} b \sin \theta db d\epsilon d\vec{v}_{\alpha} d\vec{v}_{\beta}. \end{aligned}$$

When the operators are designated by $\{ \}$, $\{ \}^r$, then

$$\begin{aligned} & \{ t^{(hk)}, t^{(hk)} \} + \frac{1}{2} \{ t^{(hk)}, t^{(hk)} \}^r = \\ & = \{ t^{(hk)}, T^{(hk)} \} + \frac{1}{2} \{ t^{(hk)}, T^{(hk)} \}^r. \end{aligned} \quad (22)$$

Utilizing (18) and (20), we obtain from equation (22) a variation principle in the form

$$\begin{aligned} & \{ T^{(hk)}, T^{(hk)} \} + \frac{1}{2} \{ T^{(hk)}, T^{(hk)} \}^r \geq \\ & \geq \{ t^{(hk)}, t^{(hk)} \} + \frac{1}{2} \{ t^{(hk)}, t^{(hk)} \}^r \geq 0. \end{aligned}$$

The best approximation is achieved when

$$\delta \sum_{\alpha} \int (t_{\alpha}^{(hk)} : R_{\alpha}^{(hk)}) d\vec{v}_{\alpha} = 0,$$

and the equations which impose limitations on the trial function have the form:

$$\begin{aligned}
(t_{\alpha}^{(hk)} : R_{\alpha}^{(hk)}) d\vec{v}_{\alpha} = \sum_j \int t_{\alpha}^{(hk)} : (t_{\alpha}^{'(hk)} + t_j^{'(hk)} - t_{\alpha}^{(hk)} - \\
- t_j^{(hk)}) P_{\alpha j}^{\alpha j} f_{\alpha}^{(0)} f_j^{(0)} g_{\alpha j} b db d\epsilon d\vec{v}_{\alpha} d\vec{v}_j + \\
+ \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \int \int \int \int \int t_{\alpha}^{(hk)} : (t_{\gamma}^{'(hk)} + t_{\delta}^{'(hk)} - t_{\alpha}^{(hk)} - \\
- t_{\beta}^{(hk)}) f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha \beta}^{\gamma \delta} g_{\alpha \beta} b \sin \theta db d\epsilon d\gamma d\vec{v}_{\alpha} d\vec{v}_{\beta}.
\end{aligned}$$

Let G_{ij} , P_{ij} be some tensor functions of velocities \vec{w}_i , \vec{w}_j . In that case, the equations in braces are defined for elastic collisions in the following form:

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$$[G_{ij}, P_{ij}]_{ij} = -\frac{1}{n_i n_j} \int \int \int \int G_{ij} : [P_{ij}' - P_{ij}] f_i^{(0)} f_j^{(0)} P_{ij}^{ij} g_{ij} b db d\epsilon d\vec{v}_i d\vec{v}_j. \quad (23)$$

Let P_{α} , P_{β} , P_{γ} , P_{δ} be tensor functions of velocities \vec{w}_{α} , \vec{w}_{β} , \vec{w}_{γ} , \vec{w}_{δ} . Then by definition the bracketed expressions for inelastic collisions will be as follows:

$$[P_{\alpha}, P_{\alpha}]_{\alpha\beta}^r = \int \int \int \int P_{\alpha} : P_{\alpha} f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta \times \quad (24)$$

$$\times db d\theta d\epsilon d\gamma d\vec{v}_{\alpha} d\vec{v}_{\beta};$$

$$[P_{\alpha}, P_{\beta}]_{\alpha\beta}^r = \int \int \int \int P_{\alpha} : P_{\beta} f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta \times \quad (25)$$

$$\times db d\theta d\epsilon d\gamma d\vec{v}_{\alpha} d\vec{v}_{\beta};$$

$$[P_{\alpha}, P_{\gamma}]_{\alpha\beta}^r = - \int \int \int \int P_{\alpha} : P_{\gamma} f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta \times \quad (26)$$

$$\times db d\theta d\epsilon d\gamma d\vec{v}_{\alpha} d\vec{v}_{\beta};$$

$$[P_{\alpha}, P_{\delta}]_{\alpha\beta}^r = - \int \int \int \int P_{\alpha} : P_{\delta} f_{\alpha}^{(0)} f_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta \times \quad (27)$$

$$\times db d\theta d\epsilon d\gamma d\vec{v}_{\alpha} d\vec{v}_{\beta}.$$

Remark 3: Assume that for the reaction to occur, molecules must collide, so that collision parameter b changes, generally speaking, with- in the limits zero to $a_{\alpha\beta} = \frac{\sigma_{\alpha} + \sigma_{\beta}}{2}$ (σ_{α} , σ_{β} are the diameters of molecules of types α and β). Integrals (24)-(27) are therefore finite.

Using definitions (23)-(27), we obtain

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$$\begin{aligned} \int t_{\alpha}^{(hk)} : R_{\alpha}^{(hk)} d\vec{v}_{\alpha} + \sum_{j=1}^{\mu} n_{\alpha} n_j [t_{\alpha}^{(hk)}, t_{\alpha}^{(hk)}]_{\alpha j} + \\ + \sum_{j=1}^{\mu} n_{\alpha} n_j [t_{\alpha}^{(hk)}, t_j^{(hk)}]_{\alpha j} + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} [t_{\alpha}^{(hk)}, t_{\alpha}^{(hk)}]_{\alpha \beta}^r + \\ + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} [t_{\alpha}^{(hk)}, t_{\beta}^{(hk)}]_{\alpha \beta}^r + \sum_{r=1}^l \sum_{\beta \gamma \delta} [t_{\alpha}^{(hk)}, t_{\gamma}^{(hk)}]_{\alpha \beta}^r = 0. \end{aligned}$$

We shall take the final combinations from Sonin polynomials as trial functions

$$t_{\alpha}^{(hk)} = w_{\alpha} \sum_{m=0}^{\xi-1} t_{\alpha m}^{(hk)} (\xi) S_n^{(m)}(W_{\alpha}^2).$$

Denoting

$$\begin{aligned} R_{\alpha m}^{(hk)} &= \int (R_{\alpha}^{(hk)} : w_{\alpha} S_n^{(m)}(W_{\alpha}^2) d\vec{v}_{\alpha}; \\ g_{\alpha, m}^{(hk)} &= \sum_{\alpha, m} t_{\alpha m}^{(hk)} R_{\alpha m}^{(hk)}. \end{aligned}$$

Then the formulation of the variation principle will acquire the following form:

$$\delta g^{(hk)} = 0,$$

If we denote

$$\begin{aligned} w_{\alpha}^{(hk)} &= \sum_{m=0}^{\xi-1} t_{\alpha m}^{(hk)} R_{\alpha m}^{(hk)} + \sum_j \sum_{m=0}^{\xi-1} \sum_{m'=0}^{\xi-1} n_{\alpha} n_j t_{\alpha m}^{(hk)} \{ t_{\alpha m'}^{(hk)} \times \\ &\times [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\alpha} S_n^{(m')}(W_{\alpha}^2)]_{\alpha j} + t_{j m'}^{(hk)} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_j \times \\ &\times S_n^{(m')}(W_j^2)]_{\alpha j} \} + \frac{1}{2} \sum_{r=1}^l \sum_{\beta \gamma \delta} \sum_{m=0}^{\xi-1} \sum_{m'=0}^{\xi-1} t_{\alpha m}^{(hk)} \{ t_{\alpha m'}^{(hk)} \times \\ &\times [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\alpha} S_n^{(m')}(W_{\alpha}^2)]_{\alpha \beta}^r + t_{\beta m'}^{(hk)} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\beta} \times \\ &\times S_n^{(m')}(W_{\beta}^2)]_{\alpha \beta}^r + 2 t_{\gamma m'}^{(hk)} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\gamma} S_n^{(m')}(W_{\gamma}^2)]_{\alpha \beta}^r \}, \end{aligned}$$

then the equations for limitations on the trial functions will have the following form

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$$w_{\alpha}^{(hk)} = 0. \quad (28)$$

We find the extremum of $g^{(hk)}$ by means of the Lagrange multipliers:

$$\frac{\partial g^{(hk)}}{\partial t_{\alpha m}^{(hk)}} + \sum_{p=1}^{\mu} \lambda_p \frac{\partial w^{(hk)}}{\partial t_{\alpha m}^{(hk)}} = 0. \quad (29)$$

It is possible to show that the consistency conditions for equations (28) and (29) are

$$\lambda_p^{(hk)} = 1, \quad p = 1, \dots, \mu.$$

If we denote

$$\begin{aligned} & \sum_l \left(n_{\alpha} n_l \{ \delta_{\alpha\beta} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\alpha} S_n^{(m')}(W_{\alpha}^2)]_{\alpha l} + \delta_{\beta l} [w_{\alpha} S_n^{(m)} \times \right. \\ & \times (W_{\alpha}^2), w_l S_n^{(m')}(W_l^2)]_{\alpha l} \} + \frac{1}{2} \sum_{\gamma \delta} \sum_{r=1}^l \{ \delta_{\alpha\beta} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\alpha} \times \\ & \times S_n^{(m')}(W_{\alpha}^2)]_{\alpha l}^r + \delta_{\beta l} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_l S_n^{(m')}(W_l^2)]_{\alpha l}^r + \\ & \left. + 2 \delta_{\beta \gamma} [w_{\alpha} S_n^{(m)}(W_{\alpha}^2), w_{\gamma} S_n^{(m')}(W_{\gamma}^2)]_{\alpha l}^r \} \right) = Q_{\alpha\beta}^{(m, m')}, \end{aligned}$$

then finding the expansion coefficients $t_{\beta m}$ is reduced to solving the following system of algebraic equations:

$$\sum_{\beta=1}^{\mu} \sum_{m'=0}^{\xi-1} Q_{\alpha\beta}^{(m, m')} t_{\beta m'}^{(hk)} = -R_{\alpha m}^{(hk)}.$$

4. Computations of Bracketed Expressions

We shall now assume that the probability densities of inelastic collision $p_{\alpha\beta}^{\gamma\delta}$ and elastic collision $p_{\alpha\beta}^{\alpha\beta}$ depend only /156 on the magnitudes of the relative velocities of the colliding molecules $g_{\alpha\beta}$. The probability densities $p_{\alpha\beta}^{\gamma\delta}, p_{\alpha\beta}^{\alpha\beta}$ are averaged over all possible orientations of a pair of colliding molecules; the possibility of the integration for ϵ (from 0 to 2π) therefore immediately arises, since

the integrand is not dependent on ϵ . In accordance with the first theory, we shall assume that the probability density $\bar{P}_{\alpha\beta}^{\gamma\delta}$ of the inelastic collision is equal to a constant $\bar{P}_{\alpha\beta}^{\gamma\delta}$, when the total translational energy of the relative motion of molecules α and β is greater than $\tilde{\epsilon}^*$; otherwise, $\bar{P}_{\alpha\beta}^{\gamma\delta}$ is equal to zero. According to the second theory, probability density $\bar{P}_{\alpha\beta}^{\gamma\delta}$ is equal to a constant $\bar{P}_{\alpha\beta}^{\gamma\delta}$ when the translational energy of the relative motion of molecules along the line of centers is greater than $\tilde{\epsilon}^*$; otherwise, $\bar{P}_{\alpha\beta}^{\gamma\delta}$ is equal to zero. As would be expected, the "elastic" bracketed expressions are expressed through the collision integrals in exactly the same manner as in a non-reacting mixture of gases. We are therefore not presenting the elastic part of the expressions within brackets here (see [1, 2]). However, the form of the collision integrals itself changes:

$$\Omega_{ij}^{(l)}(r) = \sqrt{\pi} \int_0^{\infty} e^{-g_{ij}^*} g_{ij}^{2r+2} \Phi_{ij}^{(l)} dg_{ij},$$

where

$$\Phi_{ij}^{(l)} = \int (1 - \cos^l \chi) P_{ij}^{ij} g_{ij} b db;$$

$$g_{ij}^* = g_{ij} \sqrt{\frac{m_0 M_i M_j}{2kT}}.$$

Let us now calculate the "inelastic" bracketed expressions.

1. Bracketed expressions of the type

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$$\begin{aligned} & [S_{\frac{1}{2}}^{(p)}(W_\alpha^2) \vec{W}_\alpha, S_{\frac{1}{2}}^{(q)}(W_\beta^2) \vec{W}_\beta]_{\alpha\beta}^r : \iiint S_{\frac{1}{2}}^{(p)}(W_\alpha^2) S_{\frac{1}{2}}^{(q)}(W_\beta^2) \times \\ & \times \int_{\alpha}^{(0)} \int_{\beta}^{(0)} \vec{W}_\alpha \cdot \vec{W}_\beta \bar{P}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_\alpha d\vec{v}_\beta. \end{aligned} \quad (30)$$

One can easily see that expression (30) is a coefficient of $s^p t^q$ in the expansion of the function

$$\begin{aligned} J = & \iiint \int_{\alpha}^{(0)} \int_{\beta}^{(0)} (1-s)^{-\frac{1}{2}} (1-t)^{-\frac{1}{2}} e^{-\frac{W_\alpha^2 s}{1-s}} e^{-\frac{W_\beta^2 t}{1-t}} \times \\ & \times \vec{W}_\alpha \cdot \vec{W}_\beta \bar{P}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_\alpha d\vec{v}_\beta. \end{aligned}$$

Expanding the integrands into a series in terms of s and t , we obtain

$$[S_{\frac{3}{2}}^{(p)}(W_{\alpha}^2)\vec{W}_{\alpha}, S_{\frac{3}{2}}^{(q)}(W_{\beta}^2)\vec{W}_{\beta}]_{\alpha\beta}^r = 8n_{\alpha}n_{\beta}M_{\beta}^{p+\frac{1}{2}}M_{\alpha}^{q+\frac{1}{2}}\sum_r A_{pqr}\Omega_{\alpha\beta}^r(r),$$

where

$$\Omega_{\alpha\beta}^r(r) = \sqrt{\pi} \int_{\mathcal{E}_{\alpha\beta}^*}^{\infty} e^{-\mathcal{E}_{\alpha\beta}^2} \mathcal{E}_{\alpha\beta}^{2r+2} \Phi_{\alpha\beta}^r \mathcal{E}_{\alpha\beta}^r d\mathcal{E}_{\alpha\beta}; \quad (31)$$

$$\Phi_{\alpha\beta}^r = \iiint \tilde{P}_{\alpha\beta}^r \mathcal{G}_{\alpha\beta} b \sin\theta db d\theta d\varphi. \quad (32)$$

Coefficients A_{pqr} are found from the equation

$$\sum_r A_{pqr} \mathcal{E}_{\alpha\beta}^{2r} = \sum_r \left(\frac{3}{2} - \mathcal{E}_{\alpha\beta}^2 + r \right) \frac{\mathcal{E}_{\alpha\beta}^{2r} (-1)^r (p+q)! \left(r + \frac{5}{2} + p + q - r - 1 \right)_{p+q-r}}{r! (p+q-r)! p! q!}.$$

Summation from the right is carried out under the following conditions

$$p \geq 0, \quad q \geq 0, \quad r \leq p+q.$$

As a result

$$[\vec{W}_{\alpha}, \vec{W}_{\beta}]_{\alpha\beta}^r = 8(M_{\alpha}M_{\beta})^{\frac{1}{2}} \left(\frac{3}{2} \Omega_{\alpha\beta}^r(0) - \Omega_{\alpha\beta}^r(1) \right) n_{\alpha} n_{\beta};$$

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$$\begin{aligned} [\vec{W}_{\alpha}, S_{\frac{1}{2}}^{(1)}(W_{\beta}^2)\vec{W}_{\beta}]_{\alpha\beta}^r &= \\ &= 8M_{\beta}^{\frac{1}{2}}M_{\alpha}^{\frac{1}{2}} \left(\frac{15}{4} \Omega_{\alpha\beta}^r(0) - 5\Omega_{\alpha\beta}^r(1) + \Omega_{\alpha\beta}^r(2) \right) n_{\alpha} n_{\beta}; \end{aligned}$$

$$\begin{aligned} [S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2)\vec{W}_{\alpha}, \vec{W}_{\beta}]_{\alpha\beta}^r &= \\ &= 8M_{\beta}^{\frac{1}{2}}M_{\alpha}^{\frac{1}{2}} \left(\frac{15}{4} \Omega_{\alpha\beta}^r(0) - 5\Omega_{\alpha\beta}^r(1) + \Omega_{\alpha\beta}^r(2) \right) n_{\alpha} n_{\beta}; \end{aligned}$$

$$\begin{aligned} [S_{\frac{3}{2}}^{(1)}(W_{\alpha}^2)\vec{W}_{\alpha}, S_{\frac{3}{2}}^{(1)}(W_{\beta}^2)\vec{W}_{\beta}]_{\alpha\beta}^r &= 8(M_{\alpha}M_{\beta})^{\frac{1}{2}} \left(\frac{105}{8} \Omega_{\alpha\beta}^r(0) - \right. \\ &\quad \left. - \frac{105}{4} \Omega_{\alpha\beta}^r(1) + \frac{21}{2} \Omega_{\alpha\beta}^r(2) - \Omega_{\alpha\beta}^r(3) \right) n_{\alpha} n_{\beta}. \end{aligned}$$

2. Bracketed expressions of the type

$$\begin{aligned} [S_{\frac{3}{2}}^{(p)}(W_{\alpha}^2)\vec{W}_{\alpha}, S_{\frac{3}{2}}^{(q)}(W_{\alpha}^2)\vec{W}_{\alpha}]_{\alpha\beta}^r &= \iiint S_{\frac{3}{2}}^{(p)}(W_{\alpha}^2) \times \\ &\times S_{\frac{3}{2}}^{(q)}(W_{\alpha}^2) \vec{W}_{\alpha} f_{\alpha}^{(n)} f_{\beta}^{(n)} \tilde{P}_{\alpha\beta}^r \mathcal{G}_{\alpha\beta} b \sin\theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta}. \end{aligned}$$

By expanding the integrand into a series in terms of s and t , we obtain

$$[S_{\frac{1}{2}}^{(p)}(W_{\alpha}^2)\vec{W}_{\alpha}, S_{\frac{1}{2}}^{(q)}(W_{\alpha}^2)\vec{W}_{\alpha}]_{\alpha\beta}^r = 8n_{\alpha}n_{\beta} \sum_h A_h \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(h),$$

where

$$\begin{aligned} \Phi_{pq} &= e^{-g_{\alpha\beta}^2} \sum_h A_h g_{\alpha\beta}^{2h}; \\ \Phi_{pq} &= e^{-g_{\alpha\beta}^2} \sum_{r, m, k} \left(\frac{3}{2} M_{\alpha} + g_{\alpha\beta}^2 M_{\beta} + M_{\alpha} r \right) \times \\ &\quad \frac{g_{\alpha\beta}^{2r} (-1)^m M_{\beta}^{3r+2k-m-p-q} (M_{\alpha} - M_{\beta})^{p+q-2r-k+m}}{m! (r-m)! (p+q-2r-k+m)!} \times \\ &\quad \frac{\left(r + \frac{5}{2} + k - 1\right)_k (2k+2r-p-q)!}{(2k+2r-p-q-m)! (r+k-p)! (r+k-q)!}. \end{aligned}$$

Summation is carried out under the following conditions

$$\begin{aligned} m \geq 0, \quad r \geq m, \quad p+q-2r-k+m \geq 0; \\ 2k+2r-p-q-m \geq 0, \quad r+k \geq p, \quad r+k \geq q. \end{aligned}$$

Collision integrals $\Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(h)$ are determined from formulas (31) and (32). The bracketed expressions of this type which are necessary for the calculations of transfer coefficients in the first approximation are:

$$\begin{aligned} [\vec{W}_{\alpha}, \vec{W}_{\alpha}]_{\alpha\beta}^r &= 8n_{\alpha}n_{\beta} \left(\frac{3}{2} M_{\alpha} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(0) + M_{\beta} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(1) \right); \\ [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_{\alpha}]_{\alpha\beta}^r &= [\vec{W}_{\alpha}, S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2) \vec{W}_{\alpha}]_{\alpha\beta}^r = \\ &= 8n_{\alpha}n_{\beta} \left[\frac{15}{4} M_{\alpha} M_{\beta} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(0) + \frac{5}{2} M_{\beta} (M_{\beta} - M_{\alpha}) \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(1) - M_{\beta}^2 \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(2) \right]; \\ [S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2) \vec{W}_{\alpha}, S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2) \vec{W}_{\alpha}]_{\alpha\beta}^r &= 8n_{\alpha}n_{\beta} \left[\frac{15}{4} M_{\alpha} (M_{\alpha} - M_{\beta} + \right. \\ &\quad \left. + \frac{7}{2} M_{\beta}^2) \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(0) + \frac{5}{2} M_{\beta} (3M_{\alpha} - M_{\beta} - 7M_{\alpha} M_{\beta} + \frac{7}{2} M_{\beta}^2) \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(1) + \right. \\ &\quad \left. + M_{\beta}^2 (2 + \frac{7}{2} M_{\alpha} - 7M_{\beta}) \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(2) + M_{\beta}^3 \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(3) \right]. \end{aligned}$$

3. Bracketed expressions of the type

$$\{S_{\frac{1}{2}}^{(p)}(W_{\alpha}^2)\vec{W}_{\alpha}, S_{\frac{1}{2}}^{(q)}(W_Y^2)\vec{W}_Y\}_{\alpha\beta}^r = -\int\int\int\int S_{\frac{1}{2}}^{(p)}(W_{\alpha}^2) \times \\ \times S_{\frac{1}{2}}^{(q)}(W_Y^2) \int_{\alpha}^{(0)} \int_{\beta}^{(0)} P_{\alpha\beta}^{\gamma\delta} \vec{W}_{\alpha} \cdot \vec{W}_Y g_{\alpha\beta} b \sin\theta db d\theta d\epsilon d\varphi d\vec{v}_{\alpha} d\vec{v}_{\beta}.$$

The bracketed expressions of this type can also be obtained by expanding into a series of terms in powers of $s^p t^q$. We then have

$$\{S_{\frac{1}{2}}^{(p)}(W_{\alpha}^2)\vec{W}_{\alpha}, S_{\frac{1}{2}}^{(q)}(W_Y^2)\vec{W}_Y\}_{\alpha\beta}^r = 8 n_{\alpha} n_{\beta} \sqrt{M_{\alpha} M_Y} \sum_{fh} A_{fh} \Omega_{\alpha\beta}^{\gamma\delta(f)}(h),$$

where

$$\phi_{pq} = e^{-g_{\alpha\beta}^2} \sum_{fh} A_{fh} g_{\alpha\beta}^{2h} (g_{\beta\alpha}^{\gamma} \cdot g_{\gamma\delta}^{\delta})^f.$$

Coefficient Φ_{pq} (and consequently A_{fh}) can be found from the formula /160

$$\phi_{pq} = e^{-g_{\alpha\beta}^2} \sum_{r m n i k l} \left(r+m+n+\frac{3}{2} - g_{\beta\alpha}^{\gamma} \cdot g_{\gamma\delta}^{\delta} \sqrt{\frac{M_{\beta} M_{\delta}}{M_{\alpha} M_Y}} \right) \times \\ \times \frac{g_{\alpha\beta}^{2r} (g_{\beta\alpha}^{\gamma} \cdot g_{\gamma\delta}^{\delta})^m \epsilon^n (-1)^{3m+2k+2l+2r+n+l-p-q+1}}{m! (2r+2m+n+i+k+l-p-q)!} \times \\ \times \frac{2^{p+q-r-m-n-i-k-l} (2r+2m+n+k+2l-p-q)!}{(p+q-r-2m-n-i-k-l)! k! (n-k)! i! (l-i)!} \times \\ \times \frac{\left(r+m+n+\frac{5}{2}+l-1 \right)_l^{\frac{m}{2}} M_{\alpha}^{\frac{m}{2}} M_{\beta}^{p-i-\frac{m}{2}} M_Y^{\frac{m}{2}} M_{\delta}^{-\frac{m}{2}-i+q} (M_{\beta}-M_Y)^i}{(r+m+k+l-p)! (r+m+n+l-q)!}. \quad (33)$$

Summation in expression (33) is carried out under the conditions

- a) $r \geq 0, m \geq 0, n \geq 0, i \geq 0, k \geq 0, l \geq 0, k \leq n, i \leq l$;
- b) $2r+2m+n+k+2l \geq p+q, 2r+2m+n+i+k+l \geq p+q$;
- c) $r+2m+n+k+l+i \leq p+q$;
- d) $r+m+k+l \geq p, r+m+n+l \geq q$.

Integrals $\Omega_{\alpha\beta}^{\gamma\delta(f)}(h)$ are

$$\bar{r}_{\alpha\beta}^{\gamma\delta(f)}(h) = \sqrt{\pi} \int e^{-\frac{g_{\alpha\beta}^2}{g_{\alpha\beta}^{2h+2+f} (g_{\alpha\beta}^2 - \epsilon)^{f/2}} \bar{r}_{\alpha\beta}^{\gamma\delta(f)} d g_{\alpha\beta}};$$

$$\bar{r}_{\alpha\beta}^{\gamma\delta(f)} = \iiint \bar{P}_{\alpha\beta}^{\gamma\delta} \cos^f \chi g_{\alpha\beta} \sin \theta d\theta d\varphi.$$

In these formulas, χ is the angle between the vectors $\vec{g}_{\beta\alpha}$ and $\vec{g}_{\gamma\delta}$; ϵ is the heat of the reaction

$$\epsilon = \frac{\epsilon_{\gamma} + \epsilon_{\delta} - \epsilon_{\alpha} - \epsilon_{\beta}}{kT}.$$

Let us write the following principal bracketed expressions of this type:

$$[\vec{W}_{\alpha}, \vec{W}_{\gamma}]_{\alpha\beta}^r = 8 n_{\alpha} n_{\beta} \left[\sqrt{M_{\beta} M_{\delta}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(0) - \frac{3}{2} \sqrt{M_{\alpha} M_{\gamma}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(0) \right];$$

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$$[S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2) \vec{W}_{\alpha}, \vec{W}_{\gamma}]_{\alpha\beta}^r = 8 n_{\alpha} n_{\beta} M_{\beta} \left[-\frac{15}{4} \sqrt{M_{\alpha} M_{\gamma}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(0) + \right. \\ \left. + \frac{5}{2} \sqrt{M_{\alpha} M_{\gamma}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(1) + \frac{5}{2} \sqrt{M_{\beta} M_{\delta}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(0) - \sqrt{M_{\beta} M_{\delta}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(1) \right];$$

$$[\vec{W}_{\alpha}, S_{\frac{1}{2}}^{(1)}(W_{\gamma}^2) \vec{W}_{\gamma}]_{\alpha\beta}^r = 8 n_{\alpha} n_{\beta} M_{\delta} \left[-\frac{5}{2} \left(\epsilon + \frac{3}{2} \right) \sqrt{M_{\alpha} M_{\gamma}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(0) + \right. \\ \left. + \frac{5}{2} \sqrt{M_{\alpha} M_{\gamma}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(1) + \left(\epsilon + \frac{5}{2} \right) \sqrt{M_{\beta} M_{\delta}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(0) - \sqrt{M_{\beta} M_{\delta}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(1) \right];$$

$$[S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2) \vec{W}_{\alpha}, S_{\frac{1}{2}}^{(1)}(W_{\gamma}^2) \vec{W}_{\gamma}]_{\alpha\beta}^r = 8 n_{\alpha} n_{\beta} \sqrt{M_{\alpha} M_{\gamma}} M_{\beta} M_{\delta} \left\{ \left[\frac{15}{4} \frac{M_{\beta} - M_{\gamma}}{M_{\beta} M_{\delta}} - \right. \right. \\ \left. - \frac{25}{4} \epsilon - \frac{105}{8} \right] \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(0) + \left[\frac{25}{2} + \frac{7}{2} \epsilon \right] \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(1) - \frac{7}{2} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(0)}(2) + \\ + \sqrt{\frac{M_{\beta} M_{\alpha}}{M_{\alpha} M_{\gamma}}} \left[\frac{5}{2} \epsilon + \frac{35}{4} - \frac{5}{2} \frac{M_{\beta} - M_{\gamma}}{M_{\beta} M_{\delta}} + 5 \frac{M_{\alpha} M_{\gamma}}{M_{\beta} M_{\delta}} \right] \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(0) - \\ \left. - \sqrt{\frac{M_{\beta} M_{\delta}}{M_{\alpha} M_{\gamma}}} [5 + \epsilon] \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(1) + \sqrt{\frac{M_{\beta} M_{\delta}}{M_{\alpha} M_{\gamma}}} \bar{\Omega}_{\alpha\beta}^{\gamma\delta(1)}(2) - 2 \bar{\Omega}_{\alpha\beta}^{\gamma\delta(2)}(0) \right\}.$$

4. The bracketed expressions of the type

$$[S_{s/2}^{(p)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha, S_{s/2}^{(q)}(W_\beta^2)\vec{W}_\beta^0\vec{W}_\beta]_{\alpha\beta}^r = \int \int \int \int \int S_{s/2}^{(p)}(W_\alpha^2)S_{s/2}^{(q)} \times \\ \times (W_\beta^2)\vec{W}_\alpha^0\vec{W}_\alpha : \vec{W}_\beta^0\vec{W}_\beta f_\alpha^{(0)} f_\beta^{(0)} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_\alpha d\vec{v}_\beta.$$

The bracketed expressions of this type are calculated from the formulas

$$[S_{s/2}^{(p)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha, S_{s/2}^{(q)}(W_\beta^2)\vec{W}_\beta^0\vec{W}_\beta]_{\alpha\beta} = \quad (34) \\ = \frac{16}{3} n_\alpha n_\beta M_\alpha^{p+1} M_\beta^{q+1} \sum_r A_{pq} \Omega_{\alpha\beta}^r \Upsilon_\alpha^\delta(r),$$

where

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$$\sum_r A_{pq} g_{\alpha\beta}^{2r} = \sum_r \left(g_{\alpha\beta}^4 - 5g_{\alpha\beta}^2 + \frac{15}{4} + 4r - 2g_{\alpha\beta}^2 r + \right. \\ \left. + r^2 \right) \frac{g_{\alpha\beta}^{2r} (-1)^r (p+q)! \left(r + \frac{7}{2} + p + q - r - 1 \right)}{r! (p+q-r)! p! q!} \Big|_{p+q-r}. \quad (35)$$

Summation of the right side is carried out under the conditions

$p \geq 0, q \geq 0, r \leq p+q$. Utilizing formulas (34) and (35), we find

$$[\vec{W}_\alpha^0\vec{W}_\alpha, \vec{W}_\beta^0\vec{W}_\beta]_{\alpha\beta}^r = \frac{16}{3} n_\alpha n_\beta M_\alpha M_\beta \left\{ \frac{15}{4} \Omega_{\alpha\beta}^r \Upsilon_\alpha^\delta(0) - 5 \Omega_{\alpha\beta}^r \Upsilon_\alpha^\delta(1) + \Omega_{\alpha\beta}^r \Upsilon_\alpha^\delta(2) \right\}.$$

5. Bracketed expressions of the type

$$[S_{s/2}^{(p)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha, S_{s/2}^{(q)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha]_{\alpha\beta}^r = \\ = \int \int \int \int \int S_{s/2}^{(p)}(W_\alpha^2)S_{s/2}^{(q)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha : \vec{W}_\alpha^0\vec{W}_\alpha f_\alpha^{(0)} f_\beta^{(0)} \Omega_{\alpha\beta}^r \Upsilon_\alpha^\delta g_{\alpha\beta} \times \\ \times b \sin \theta db d\theta d\epsilon d\varphi d\vec{v}_\alpha d\vec{v}_\beta$$

can be found from the following formula

$$[S_{s/2}^{(p)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha, S_{s/2}^{(q)}(W_\alpha^2)\vec{W}_\alpha^0\vec{W}_\alpha]_{\alpha\beta}^r = \frac{16}{3} n_\alpha n_\beta \sum_h A_h \Omega_{\alpha\beta}^r \Upsilon_\alpha^\delta(h),$$

where

$$\Phi_{pq} = e^{-g_{\alpha\beta}^2} \sum_h A_h g_{\alpha\beta}^{2h}; \\ \Phi_{pq} = e^{-g_{\alpha\beta}^2} \sum_{r m k} \left(\frac{15}{4} M_\alpha^2 + 5M_\alpha M_\beta g_{\alpha\beta}^2 - g_{\alpha\beta}^4 M_\beta^2 + (4M_\alpha^2 + \right. \quad (36)$$

$$\begin{aligned}
& + 2M_{\beta} g_{\alpha\beta}^2 r + M_{\alpha}^2 r^2 \left) \frac{g_{\alpha\beta}^{2r} 2^{r-m} (-1)^m M_{\beta}^{3r+2k-m-p-q}}{m! (r-m)! (p+q-2r-k+m)!} \times \\
& \times \frac{(M_{\alpha} - M_{\beta})^{p+q-2r-k+m} \left(r + \frac{7}{2} + k - 1 \right)_k (2k+2r-p-q)!}{(2k+2r-p-q-m)! (r+k-p)! (r+k-q)!}.
\end{aligned}
\tag{36 continued}$$

Summation is carried out under the conditions

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$$\left. \begin{aligned} r \geq 0, \quad m \geq 0, \quad k \geq 0, \quad m \leq r, \quad r+k \geq p, \quad r+k \geq q, \\ 2r+k-m \leq p+q, \quad 2k+2r-m \geq p+q. \end{aligned} \right\} \tag{37}$$

Utilizing formulas (36) and (37), we obtain

$$\begin{aligned}
[\vec{W}_{\alpha}^0 \vec{W}_{\alpha}, \vec{W}_{\alpha}^0 \vec{W}_{\alpha}]_{\alpha\beta}^r = \frac{16}{3} n_{\alpha} n_{\beta} \left[\frac{15}{4} M_{\alpha}^2 \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(0) + \right. \\
\left. + 5 M_{\alpha} M_{\beta} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(1) - M_{\beta}^2 \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta}(2) \right].
\end{aligned}$$

6. Bracketed expressions of the type

$$\begin{aligned}
[S_{s/2}^{(p)} (W_{\alpha}^2) \vec{W}_{\alpha}^0 \vec{W}_{\alpha}, S_{s/2}^{(q)} (W_Y^2) \vec{W}_Y^0 \vec{W}_Y]_{\alpha\beta}^r = - \iiint S_{s/2}^{(p)} (W_{\alpha}^2) S_{s/2}^{(q)} (W_Y^2) \vec{W}_{\alpha}^0 \vec{W}_{\alpha} : \vec{W}_Y^0 \vec{W}_Y f_{\alpha}^{(0)} f_{\beta}^{(0)} g_{\alpha\beta} \times \\
\times P_{\alpha\beta}^r \sin \Theta \, d\Theta \, d\Omega \, d\epsilon \, d\varphi \, d\vec{v}_{\alpha} \, d\vec{v}_{\beta}.
\end{aligned}$$

For calculating of the viscosity in the first approximation, we require only a bracketed expression of the given type when $p = q = 0$:

$$\begin{aligned}
[\vec{W}_{\alpha}^0 \vec{W}_{\alpha}, \vec{W}_Y^0 \vec{W}_Y]_{\alpha\beta}^r = -8 n_{\alpha} n_{\beta} M_{\alpha} M_Y \left[\frac{5}{2} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta(0)}(0) + \right. \\
+ \frac{1}{3} \frac{M_{\beta} M_{\delta}}{M_{\alpha} M_Y} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta(0)}(1) - \frac{1}{3} \frac{M_{\beta} M_{\delta}}{M_{\alpha} M_Y} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta(0)}(2) - \\
\left. - \frac{10}{3} \sqrt{\frac{M_{\beta} M_{\delta}}{M_{\alpha} M_Y}} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta(1)}(1) + \frac{M_{\beta} M_{\delta}}{M_{\alpha} M_Y} \Omega_{\alpha\beta}^r Y_{\alpha\beta}^{\delta(2)}(0) \right].
\end{aligned}$$

5. Calculation of Collision Integrals

It follows from the foregoing discussion that in order to find transfer coefficients, collision integrals of three types must be calculated:

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$$\begin{aligned}
 1) \quad \Omega_{ij}^{(l)}(r) &= \sqrt{\pi} \int e^{-g_{ij}^2} g_{ij}^{2r+2} \Phi_{ij}^{(l)} dg_{ij}; \\
 \Phi_{ij}^{(l)} &= \int (1 - \cos^l \chi) P_{ij}^{ij} g_{ij} db; \\
 2) \quad \left. \begin{aligned} \Omega_{\alpha\beta}^{r\gamma\delta} &= \sqrt{\pi} \int e^{-g_{\alpha\beta}^2} g_{\alpha\beta}^{2r+2} \Phi_{\alpha\beta}^{r\gamma\delta} dg_{\alpha\beta}; \\ \Phi_{\alpha\beta}^{r\gamma\delta} &= \iiint P_{\alpha\beta}^{r\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\varphi; \end{aligned} \right\} \quad (38) \\
 3) \quad \Omega_{\alpha\beta}^{r\gamma\delta(f)}(h) &= \sqrt{\pi} \int e^{-g_{\alpha\beta}^2} g_{\alpha\beta}^{2h+2+f} (g_{\alpha\beta}^2 - \varepsilon)^{\frac{f}{2}} \Phi_{\alpha\beta}^{r\gamma\delta} dg_{\alpha\beta}; \\
 \Phi_{\alpha\beta}^{r\gamma\delta} &= \iiint P_{\alpha\beta}^{r\gamma\delta} \cos^f \chi g_{\alpha\beta} b \sin \theta db d\theta d\varphi.
 \end{aligned}$$

Collision Integrals of the First Type

Let us calculate collision integrals of this type by using, for example, the model of solid elastic spheres. The geometric collision parameters are shown in Figure 2.

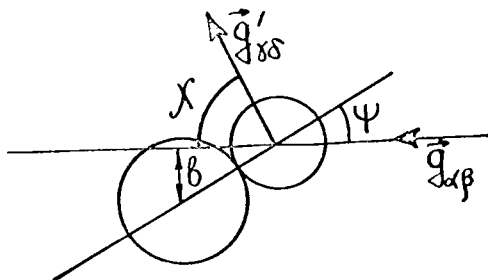


Figure 2: Changes of the relative velocity of molecules during inelastic collisions.

$$\frac{1}{2} \frac{m_i m_j}{m_i + m_j} g_{ij}^2 < \frac{1}{2} \frac{m_i m_j}{m_i + m_j} g_{ij}^{*2} \quad \text{or} \quad g_{ij} < g_{ij}^*.$$

In this case

$$\begin{aligned} \Phi_{ij}^{(l)} &= \frac{\sigma_{ij}^2}{4} p_{ij} g_{ij} \left[2 - \frac{1}{l+1} (1 + (-1)^l) \right]; \\ \Omega_{ij}^{(l)}(r) &= \frac{\pi \sigma_{ij}^2}{2} p_{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - \frac{1 + (-1)^l}{2(l+1)} \right] \left\{ (r+1)! - e^{-g_{ij}^{*2}} [g_{ij}^{*2(r+1)} + \right. \\ &\quad \left. + (r+1)g_{ij}^{*2r} + (r+1)rg_{ij}^{*2(r-1)} + \dots + (r+1)!g_{ij}^{*2} + (r+1)!] \right\}, \end{aligned}$$

where

$$g_{ij}^* = \sqrt{\frac{m_0 M_i M_j}{2kT}} g_{ij}. \quad (39)$$

Second theory. The whole integration domain is subdivided into two regions: the first being $g_{ij} < g_{ij}^*$, $0 \leq \chi \leq \pi$; the second being

$$g_{ij} \geq g_{ij}^*; \quad 0 \leq \chi \leq 2 \arcsin g_{ij}^* / g_{ij}.$$

By performing integration we find

$$\begin{aligned} \Omega_{ij}^{(l)}(r) &= \frac{\pi \sigma_{ij}^2}{2} p_{ij} \sqrt{\frac{kT}{2\pi\mu}} \left\{ \left[1 + \frac{1 + (-1)^l}{2(l+1)} \right] \left[(r+1)! - \right. \right. \\ &\quad \left. - e^{-g_{ij}^{*2}} (g_{ij}^{*2(r+1)} + (r+1)g_{ij}^{*2r} + (r+1)rg_{ij}^{*2(r-1)} + \dots \right. \\ &\quad \left. \left. + (r+1)!g_{ij}^{*2} + (r+1)!) \right] + e^{-g_{ij}^{*2}} \sum_{\beta=2}^{l+1} \frac{2^{\beta-1} (-1)^\beta l!}{\beta! (l+1-\beta)!} \times \right. \\ &\quad \times [g_{ij}^{*2(r+1)} + (r+1-\beta)g_{ij}^{*2r} + (r+1-\beta)(r-\beta)g_{ij}^{*2(r-1)} + \dots \\ &\quad \left. \left. + (r+1-\beta)!g_{ij}^{*2(\beta+1)} + (r+1-\beta)!g_{ij}^{*2\beta}] \right\}. \end{aligned} \quad (40)$$

Using formulas (39) and (40), it is easy to obtain formulas for integrals which are necessary in calculating transfer coefficients in the first approximation.

First theory.

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$$\begin{aligned}\Omega_{ij}^{(1)}(1) &= \pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} \left(\frac{1}{2} g_{ij}^{*4} + g_{ij}^{*2} + 1 \right) \right]; \\ \Omega_{ij}^{(2)}(2) &= 2\pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} \left(\frac{1}{6} g_{ij}^{*6} + \frac{1}{2} g_{ij}^{*4} + g_{ij}^{*2} + 1 \right) \right]; \\ \Omega_{ij}^{(1)}(2) &= 3\pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} \left(\frac{1}{6} g_{ij}^{*6} + \frac{1}{2} g_{ij}^{*4} + g_{ij}^{*2} + 1 \right) \right]; \\ \Omega_{ij}^{(1)}(3) &= 12\pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} \left(\frac{1}{24} g_{ij}^{*8} + \frac{1}{6} g_{ij}^{*6} + \frac{1}{2} g_{ij}^{*4} + g_{ij}^{*2} + 1 \right) \right].\end{aligned}$$

Second theory.

$$\begin{aligned}\Omega_{ij}^{(1)}(1) &= \pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} (g_{ij}^{*2} + 1) \right]; \\ \Omega_{ij}^{(2)}(2) &= 2\pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} (g_{ij}^{*2} + 1) \right]; \\ \Omega_{ij}^{(1)}(2) &= 3\pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} \left(\frac{1}{3} g_{ij}^{*4} + g_{ij}^{*2} + 1 \right) \right]; \\ \Omega_{ij}^{(1)}(3) &= 12\pi \sigma_{ij}^2 p_{ij}^{ij} \sqrt{\frac{kT}{2\pi\mu}} \left[1 - e^{-g_{ij}^{*2}} \left(\frac{1}{12} g_{ij}^{*6} + \frac{5}{12} g_{ij}^{*4} + g_{ij}^{*2} + 1 \right) \right].\end{aligned}$$

Collision Integrals of the Third Type

For calculating collision integrals of the third type it is necessary to know the probability of inelastic

collisions $\bar{p}_{\alpha\beta}^{\gamma\delta}$ as a function of the angles θ and φ .

Since such information for chemical reactions is presently unavailable,

we shall assume that the scattering of particles is isotropic. We can assume that collision of particles α and β with the appropriate energies leads to the formation of an activated complex $(\alpha\beta)^\ddagger$, the dissociation of which $(\alpha\beta)^\ddagger \rightarrow \gamma + \delta$ leads to the scattering of particles in random directions. Thus, the probability of the scattering of particles in the solid angle $d\Omega(\theta, \varphi)$ is independent of the coordinates θ and φ ; it depends only on the solid angle.

Then $\bar{p}_{\alpha\beta}^{\gamma\delta}$ is only a function of $g_{\alpha\beta}$. Thus, formula (38)

is reduced to the following form:

$$\bar{\Phi}_{\alpha\beta}^{\gamma\delta} = (-1)^f \bar{p}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} \int \sin^{f+1} \theta \cos^f \varphi \, d\theta \, d\varphi. \quad (41)$$

Remark 4: It follows from formula (41) that within the framework of the theory of isotropic scattering all collision integrals of the form $\bar{\Omega}_{\alpha\beta}^{\gamma\delta(2m+1)}(h)$ are identically equal to zero.

By performing the corresponding integration we obtain the following:

First theory.

$$\begin{aligned} \bar{\Phi}_{\alpha\beta}^{\gamma\delta} &= 4(-1)^f \bar{p}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta}^2 \sigma_{\alpha\beta}^2 \sum_{n=0}^{f/2} \frac{(-1)^n (f/2)!}{n! \left(\frac{f}{2} - n\right)! (2n+1)} \times \sum_{p=0}^{\infty} \frac{(-1)^p}{p!} \times \frac{m(m-1) \dots (m-p+1)}{2p+1}, \quad m = \frac{f-1}{2}; \\ \bar{\Omega}_{\alpha\beta}^{\gamma\delta(2k)}(h) &= 2 \sqrt{\frac{2\pi k T}{\mu}} \bar{p}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta}^2 \sigma_{\alpha\beta}^2 \sum_{n=0}^k \frac{(-1)^n k!}{n! (k-n)! (2n+1)} \times \sum_{p=0}^{\infty} \frac{(-1)^p k(k-1) \dots (k-p+1)}{p! (2p+1)} \left\{ \sum_{q=0}^k \frac{\varepsilon^q (-1)^q k!}{q! (k-q)!} e^{-\varepsilon_{\alpha\beta}^2} \times \right. \\ &\quad \times [g_{\alpha\beta}^{*2(h+2k-q+1)} + (h+2k+1-q)g_{\alpha\beta}^{*2(h+2k-q)} + (h+2k-q+1)(h+ \\ &\quad \left. + 2k-q)g_{\alpha\beta}^{*2(h+2k-q-1)} + \dots + (h+2k-q+1)!g_{\alpha\beta}^{*2} + (h+2k-q+1)! \right\}; \end{aligned}$$

Second theory.

$$\begin{aligned} \bar{\Phi}_{\alpha\beta}^{\gamma\delta} &= 4 \bar{p}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta}^2 \sigma_{\alpha\beta}^2 \sum_{n=0}^{f/2} \frac{(-1)^n (f/2)!}{n! \left(\frac{f}{2} - n\right)! (2n+1)} \times \\ &\quad \times \sum_{p=0}^{\infty} \frac{(-1)^p m(m-1) \dots (m-p+1)}{p! (2p+1)} - g_{\alpha\beta} (1 - g_{\alpha\beta}^{*2} / g_{\alpha\beta}^2); \end{aligned}$$

$$\begin{aligned} \Omega_{\alpha\beta}^{\gamma\delta(2k)}(h) &= 2p_{\alpha\beta}^{\gamma\delta} \frac{2}{\alpha\beta} \sqrt{\frac{2\pi kT}{\mu}} \sum_{n=0}^k \frac{(-1)^n k!}{n!(k-n)!(2n+1)} \times \\ &\times \sum_{p=0}^{\infty} \frac{(-1)^p \left(k - \frac{1}{2}\right) \left(k - \frac{1}{2} - 1\right) \dots \left(k - \frac{1}{2} - p + 1\right)}{p!(2p+1)} \frac{k}{q!} \frac{\varepsilon^q (-1)^q k!}{q!(k-q)!} \times \\ &\times \{ g_{\alpha\beta}^{*2(h+2k-q)} + 2(h+2k-q) g_{\alpha\beta}^{*2(h+2k-q-1)} + 3(h+ \\ &+ 2k-q)(h+2k-q-1) g_{\alpha\beta}^{*2(h+2k-q-2)} + \dots + (h+2k-q+1)! \} e^{-g_{\alpha\beta}^{*2}}. \end{aligned}$$

Let us present specific formulas for calculating lower-order collision integrals:

First theory.

$$\begin{aligned} \Omega_{\alpha\beta}^{\gamma\delta(0)}(0) &= \pi \sqrt{\frac{2\pi kT}{\mu}} p_{\alpha\beta}^{\gamma\delta} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*2} + 1); \\ \Omega_{\alpha\beta}^{\gamma\delta(0)}(1) &= \pi \sqrt{\frac{2\pi kT}{\mu}} p_{\alpha\beta}^{\gamma\delta} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*4} + 2g_{\alpha\beta}^{*2} + 2); \\ \Omega_{\alpha\beta}^{\gamma\delta(0)}(2) &= \pi \sqrt{\frac{2\pi kT}{\mu}} p_{\alpha\beta}^{\gamma\delta} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*6} + 3g_{\alpha\beta}^{*4} + 6g_{\alpha\beta}^{*2} + 6); \\ \Omega_{\alpha\beta}^{\gamma\delta(2)}(0) &= \frac{\pi}{3} \sqrt{\frac{2\pi kT}{\mu}} p_{\alpha\beta}^{\gamma\delta} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} [g_{\alpha\beta}^{*6} + (3-\varepsilon)(g_{\alpha\beta}^{*4} + 2g_{\alpha\beta}^{*2} + 2)], \end{aligned}$$

here

$$\varepsilon = (\varepsilon_Y + \varepsilon_\delta - \varepsilon_\alpha - \varepsilon_\beta)/kT;$$

Second theory.

$$\begin{aligned} \Omega_{\alpha\beta}^{\gamma\delta(0)}(0) &= \pi \sigma_{\alpha\beta}^2 p_{\alpha\beta}^{\gamma\delta} \sqrt{\frac{2\pi kT}{\mu}} e^{-g_{\alpha\beta}^{*2}}; \\ \Omega_{\alpha\beta}^{\gamma\delta(0)}(1) &= \pi \sigma_{\alpha\beta}^2 p_{\alpha\beta}^{\gamma\delta} \sqrt{\frac{2\pi kT}{\mu}} e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*2} + 2); \\ \Omega_{\alpha\beta}^{\gamma\delta(0)}(2) &= \pi \sigma_{\alpha\beta}^2 p_{\alpha\beta}^{\gamma\delta} \sqrt{\frac{2\pi kT}{\mu}} e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*4} + 4g_{\alpha\beta}^{*2} + 6); \end{aligned}$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(2) = \frac{\pi}{3} \sigma_{\alpha\beta}^2 \frac{\gamma\delta}{\rho_{\alpha\beta}} \sqrt{\frac{2\pi kT}{\mu}} e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*4} + (4-\epsilon)g_{\alpha\beta}^{*2} + 6-2\epsilon).$$

Collision Integrals of the Second Type

Within the framework of the theory of isotropic scattering, these integrals can easily be found as special cases of the above-presented formulas for the calculation of the collision integrals of the third type (in these formulas, it is only necessary to assume $f = 0$, $k = 0$).

Isotropic scattering, first theory.

$$\Omega_{\alpha\beta}^{\gamma\delta}(0) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*2} + 1);$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(1) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*4} + 2g_{\alpha\beta}^{*2} + 2);$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(2) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*6} + 3g_{\alpha\beta}^{*4} + 6g_{\alpha\beta}^{*2} + 6);$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(3) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*8} + 4g_{\alpha\beta}^{*6} + 12g_{\alpha\beta}^{*4} + 24g_{\alpha\beta}^{*2} + 24).$$

Isotropic scattering, second theory.

$$\Omega_{\alpha\beta}^{\gamma\delta}(0) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}};$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(1) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*2} + 2);$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(2) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*4} + 4g_{\alpha\beta}^{*2} + 6);$$

$$\Omega_{\alpha\beta}^{\gamma\delta}(3) = \pi \sqrt{\frac{2\pi kT}{\mu}} \frac{\gamma\delta}{\rho_{\alpha\beta}} \sigma_{\alpha\beta}^2 e^{-g_{\alpha\beta}^{*2}} (g_{\alpha\beta}^{*6} + 6g_{\alpha\beta}^{*4} + 18g_{\alpha\beta}^{*2} + 24).$$

It is possible to show that phenomenological notation of the transfer coefficients in the form of the ratio of the determinants is the same as in a nonreacting gas. However, elements of the determinants change. When chemical reactions do not take place in a gas mixture, or when their effect is negligible ($e^{g*2\alpha\beta} \gg 1$), the formulas presented below for transfer coefficients coincide with the corresponding formulas for transfer coefficients in a nonreacting gas mixture.

1. Viscosity coefficient:

$$\eta = \frac{\begin{vmatrix} H_{11}, & \dots, & H_{1\mu}, & n_1/n \\ \dots & \dots & \dots & \dots \\ H_{\mu 1}, & \dots, & H_{\mu\mu}, & n_\mu/n \\ n_1/n, & \dots, & n_\mu/n, & 0 \end{vmatrix}}{\begin{vmatrix} H_{11}, & \dots, & H_{1\mu} \\ \dots & \dots & \dots \\ H_{\mu 1}, & \dots, & H_{\mu\mu} \end{vmatrix}},$$

here

$$H_{\alpha\beta} = \frac{2Q_{\alpha\beta}^{00}}{5n^2kT};$$

$$Q_{\alpha\beta}^{00} = \sum_l \left(n_\alpha n_l \{ \delta_{\alpha\beta} [w_\alpha, w_\alpha]_{\alpha l} + \delta_{\beta l} [w_\alpha, w_l]_{\alpha l} \} + \right. \\ \left. + \frac{1}{2} \sum_{\gamma} \sum_{r=1}^l \{ \delta_{\alpha\beta} [w_\alpha, w_\alpha]_{\alpha l}^r + \delta_{\beta l} [w_\alpha, w_l]_{\alpha l}^r + 2\delta_{\beta\gamma} [w_\alpha, w_\gamma]_{\alpha l}^r \} \right),$$

$$w_\alpha = \vec{w}_\alpha^0 \vec{w}_\alpha = \vec{w}_\alpha \vec{w}_\alpha - \frac{1}{3} w_\alpha^2 U.$$

$$\lambda' = -\frac{75}{8} k^2 T \frac{\begin{vmatrix} q_{11}^{00}, \dots, q_{1\mu}^{00}, q_{11}^{01}, \dots, q_{1\mu}^{01}, 0 \\ \dots \\ q_{\mu 1}^{00}, \dots, q_{\mu\mu}^{00}, q_{\mu 1}^{01}, \dots, q_{\mu\mu}^{01}, 0 \\ q_{11}^{10}, \dots, q_{1\mu}^{10}, q_{11}^{11}, \dots, q_{1\mu}^{11}, 1 \\ \dots \\ q_{\mu 1}^{10}, \dots, q_{\mu\mu}^{10}, q_{\mu 1}^{11}, \dots, q_{\mu\mu}^{11}, 1 \\ 0, \dots, 0, 1, \dots, 1, 0 \end{vmatrix}}{\begin{vmatrix} q_{11}^{00}, \dots, q_{1\mu}^{00}, q_{11}^{01}, \dots, q_{1\mu}^{01} \\ \dots \\ q_{\mu 1}^{00}, \dots, q_{\mu\mu}^{00}, q_{\mu 1}^{01}, \dots, q_{\mu\mu}^{01} \\ q_{11}^{10}, \dots, q_{1\mu}^{10}, q_{11}^{11}, \dots, q_{1\mu}^{11} \\ \dots \\ q_{\mu 1}^{10}, \dots, q_{\mu\mu}^{10}, q_{\mu 1}^{11}, \dots, q_{\mu\mu}^{11} \end{vmatrix}}$$

here

$$q_{\alpha\beta}^{mm'} = \tilde{Q}_{\alpha\beta}^{mm'} \frac{\sqrt{m_\alpha m_\beta}}{n_\alpha n_\beta}; \quad (42)$$

$$\begin{aligned} \tilde{Q}_{\alpha\beta}^{00} = & \sum_{l=1}^{\mu} \left(n_\alpha n_l \left\{ [\vec{W}_\alpha, \vec{W}_\alpha]_{\alpha l} \left(\delta_{\alpha\beta} - \frac{n_\beta \sqrt{m_\beta}}{n_\alpha \sqrt{m_\alpha}} \right) + [\vec{W}_\alpha, \vec{W}_l]_{\alpha l} \left(\delta_{\beta l} - \right. \right. \right. \\ & \left. \left. - \delta_{\alpha l} \frac{\sqrt{m_\beta} n_\beta}{\sqrt{m_\alpha} n_\alpha} \right) \right\} + \frac{1}{2} \sum_{\gamma} \sum_{r=1}^l \left\{ [\vec{W}_\alpha, \vec{W}_\alpha]_{\alpha l}^r \left(\delta_{\alpha\beta} - \frac{n_\beta \sqrt{m_\beta}}{n_\alpha \sqrt{m_\alpha}} \right) + [\vec{W}_\alpha, \vec{W}_l]_{\alpha l}^r \left(\delta_{\beta l} - \right. \right. \\ & \left. \left. - \delta_{\alpha l} \frac{n_\beta \sqrt{m_\beta}}{n_\alpha \sqrt{m_\alpha}} \right) + 2 [\vec{W}_\alpha, \vec{W}_\gamma]_{\alpha l}^r \left(\delta_{\beta\gamma} - \delta_{\alpha\gamma} \frac{\sqrt{m_\beta} n_\beta}{\sqrt{m_\alpha} n_\alpha} \right) \right\} \right); \end{aligned}$$

$$\begin{aligned}
 \tilde{Q}_{\alpha\beta}^{01} = & \sum_l^{\mu} \left(n_{\alpha} n_l \{ \delta_{\alpha\beta} [\vec{W}_{\alpha}, \vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2)]_{\alpha l} + \delta_{\beta l} [\vec{W}_{\alpha}, \vec{W}_l \right. \\
 & \times S_{\frac{1}{2}}^{(1)}(W_l^2)]_{\alpha l} \} + \frac{1}{2} \sum_Y \sum_{r=1}^l \{ \delta_{\alpha\beta} [\vec{W}_{\alpha}, \vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2)]_{\alpha l}^r + \\
 & \left. + \delta_{\beta l} [\vec{W}_{\alpha}, \vec{W}_l S_{\frac{1}{2}}^{(1)}(W_l^2)]_{\alpha l}^r + 2\delta_{\beta Y} [\vec{W}_{\alpha}, \vec{W}_Y S_{\frac{1}{2}}^{(1)}(W_Y^2)]_{\alpha l}^r \} \right); \quad (43)
 \end{aligned}$$

$$\begin{aligned}
 Q_{\alpha\beta}^{10} = & \sum_l \left(n_{\alpha} n_l \{ \delta_{\alpha\beta} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_{\alpha}]_{\alpha l} + \right. \\
 & \left. + \delta_{\beta l} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_l]_{\alpha l} \} + \right. \\
 & \left. - \frac{1}{2} \sum_Y \sum_{r=1}^l \{ \delta_{\alpha\beta} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_{\alpha}]_{\alpha l}^r + \right. \\
 & \left. + \delta_{\beta l} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_l]_{\alpha l}^r + 2\delta_{\beta Y} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_Y]_{\alpha l}^r \} \right); \quad (44)
 \end{aligned}$$

$$\begin{aligned}
 \tilde{Q}_{\alpha\beta}^{11} = & \sum_l \left(n_{\alpha} n_l \{ \delta_{\alpha\beta} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2)]_{\alpha l} + \right. \\
 & \left. + \delta_{\beta l} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_l S_{\frac{1}{2}}^{(1)}(W_l^2)]_{\alpha l} \} + \right. \\
 & \left. + \frac{1}{2} \sum_Y \sum_{r=1}^l \{ \delta_{\alpha\beta} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2)]_{\alpha l}^r + \right. \\
 & \left. + \delta_{\beta l} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_l S_{\frac{1}{2}}^{(1)}(W_l^2)]_{\alpha l}^r + \right. \\
 & \left. + 2\delta_{\beta Y} [\vec{W}_{\alpha} S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), \vec{W}_Y S_{\frac{1}{2}}^{(1)}(W_Y^2)]_{\alpha l}^r \} \right). \quad (45)
 \end{aligned}$$

3. Thermal diffusion coefficient

$$D_{\alpha}^T = n_{\alpha} \sqrt{\frac{m_{\alpha} k T}{2}}$$

where $R_{\alpha 1} = \frac{15}{4} \sqrt{\frac{2kT}{m\alpha}} n_{\alpha}$, $\tilde{Q}_{\alpha\beta}^{mm'}$ ($m, m' = 0, 1$) is calculated from formulas (42)-(45).

4. Diffusion coefficient

$$D_{\beta h} = \frac{3 k T \rho n_{\beta}}{2 n m_h \sqrt{m_{\beta}}} \cdot \left| \begin{array}{cccc} \tilde{Q}_{11}^{00}, & \tilde{Q}_{12}^{00}, & \dots, & \tilde{Q}_{1, \beta-1}^{00}, \frac{\delta_{1\beta} - \delta_{1h}}{\sqrt{m_1}}, \tilde{Q}_{1, \beta+1}^{00}, \dots, \tilde{Q}_{1\mu}^{00} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \tilde{Q}_{\mu 1}^{00}, & \tilde{Q}_{\mu 2}^{00}, & \dots, & \tilde{Q}_{\mu, \beta-1}^{00}, \frac{\delta_{\mu\beta} - \delta_{\mu h}}{\sqrt{m_{\mu}}}, \tilde{Q}_{\mu, \beta+1}^{00}, \dots, \tilde{Q}_{\mu\mu}^{00} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \tilde{Q}_{\mu 1}^{00}, & \dots & \dots & \dots & \dots & \tilde{Q}_{\mu\mu}^{00} \end{array} \right|$$

Coefficients $\tilde{Q}_{\alpha\beta}^{00}$ can be found from formula (42). Note that $\tilde{Q}_{\alpha\alpha}^{00}=0$.

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PERTURBATION OF THE MAXWELLIAN DISTRIBUTION
IN CHEMICALLY REACTING GAS MIXTURES

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The situation wherein the number of inelastic collisions is of a comparable order of magnitude as the number of elastic collisions was considered in [1]. Here we shall consider the other limiting case, the situation in which inelastic collisions occur significantly less frequently than elastic ones. The notation used here is identical to the notation used in [1]. The first approximation of the general solution of the Boltzmann equation contains an additional scalar term, $f_{\alpha}^{(0)} t_{\alpha}$. The integral equation for determining t_{α} is as follows:

$$\begin{aligned} f_{\alpha}^{(0)} \left\{ \frac{K_{\alpha}^{(0)}}{n_{\alpha}} + \frac{1}{p} \left(1 - \frac{2}{3} W_{\alpha}^2 \right) \sum_{i=1}^{\mu} m_i K_i^{(0)} \hat{U}_i^{(0)} \right\} - \\ - \frac{1}{2} \sum_r \sum_{\beta \gamma \delta} \iiint (f_{\gamma}^{(0)} f_{\delta}^{(0)} - f_{\alpha}^{(0)} f_{\beta}^{(0)}) P_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\varepsilon d\varphi d\vec{v}_{\beta} = \\ = \sum_{j=1}^{\mu} \iiint (t_{\alpha}' + t_j' - t_{\alpha} - t_j) f_{\alpha}^{(0)} f_j^{(0)} g_{\alpha j} P_{\alpha j}^{\alpha j} b db d\varepsilon d\vec{v}_j. \end{aligned} \quad (1)$$

The solution of (1) is found in the form of a series of Sonin polynomials:

$$t_{\alpha} = \sum_{m=0}^{\xi-1} t_{\alpha m}(\xi) S_{\frac{1}{2}}^{(m)}(W_{\alpha}^2). \quad (2)$$

If necessary, in equation (1) one can take into account a term of the type $J(f_{\alpha}^{(0)} f_{\alpha}^{(1)})$, as was done in [1]; here, however, we shall be interested primarily in the rate of convergence of series (2). The concentration, the mean mass velocity and the temperature of the mixture are determined in an ordinary fashion:

$$\int f_{\alpha}^{(0)} d\vec{v}_{\alpha} = n_{\alpha}, \quad (3) \quad \text{176}$$

$$\sum_{\alpha} \int m_{\alpha} f_{\alpha}^{(0)} \vec{V}_{\alpha} d\vec{v}_{\alpha} = \rho \vec{v}_0;$$

$$\frac{1}{2} \sum_{\alpha} m_{\alpha} \int V_{\alpha}^2 f_{\alpha}^{(0)} d\vec{v}_{\alpha} = \frac{3}{2} nkT. \quad (3 \text{ continued})$$

In the first approximation

$$\begin{aligned} \int f_{\alpha}^{(1)} d\vec{v}_{\alpha} &= 0; \\ \sum_{\alpha} \int m_{\alpha} f_{\alpha}^{(1)} \vec{V}_{\alpha} d\vec{v}_{\alpha} &= 0; \end{aligned} \quad (4)$$

$$\frac{1}{2} \sum_{\alpha} m_{\alpha} \int V_{\alpha}^2 f_{\alpha}^{(1)} d\vec{v}_{\alpha} = 0. \quad (5)$$

Condition (3) is fulfilled, since the integrand is odd with respect to \vec{V}_{α} . Conditions (4) and (5) imply that

$$t_{\alpha 0} = 0; \quad (6)$$

$$\sum_{\alpha} t_{\alpha 1} n_{\alpha} = 0. \quad (7)$$

Let us define the temperature of the component α by the following relationship:

$$T_{\alpha} = \frac{1}{3kn_{\alpha}} \int m_{\alpha} V_{\alpha}^2 f_{\alpha} d\vec{v}_{\alpha}.$$

Then, in the first approximation, $T_{\alpha} = T(1 - t_{\alpha 1})$. Let us, therefore, calculate the nonequilibrium partial statistical pressure of ponent α :

$$p_{\alpha} = n_{\alpha} kT + \frac{1}{3} \sum_{\alpha} m_{\alpha} \int t_{\alpha} f_{\alpha}^{(0)} V_{\alpha}^2 d\vec{v}_{\alpha} = n_{\alpha} kT(1 - t_{\alpha 1}).$$

Thus, Dalton's law has the form $p_{\alpha} = n_{\alpha} kT$. Let us note that the total pressure of the mixture $p = \sum_{\alpha} p_{\alpha} = \sum_{\alpha} n_{\alpha} kT(1 - t_{\alpha 1}) = nkT$ does not change.

Applying the variation principle (see [2]), for the determining the

expansion coefficients of (2) we obtain an infinite system of linear algebraic equations:

$$\sum_{j=1}^{\mu} \sum_{m'=0}^{\xi-1} Q_{\alpha j}^{m, m'} t_{jm'}(\xi) = -R_{\alpha m}, \quad (8) \quad \underline{177}$$

where

$$Q_{\alpha j}^{m, m'} = \sum_l n_{\alpha} n_l \{ \delta_{\alpha j} [S_{\frac{1}{2}}^{(m)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(m')}(W_{\alpha}^2)]_{\alpha l} + \\ + \delta_{jl} [S_{\frac{1}{2}}^{(m)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(m')}(W_l^2)]_{\alpha l} \}; \\ R_{\alpha m} = \int R_{\alpha}(W_{\alpha}^2) S_{\frac{1}{2}}^{(m)}(W_{\alpha}^2) d\vec{v}_{\alpha},$$

where $R_{\alpha}(W_{\alpha}^2)$ is the left-hand side of equation (1). System (8) is solved for $\mu+1$ additional conditions (6) and (7); this insures the existence of a unique solution. Let us present the ratios for calculating the bracketed expressions on the right-hand side of equation (1):

$$[S_{\frac{1}{2}}^{(0)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(m)}(W_{\alpha}^2)]_{\alpha l} = \\ = [S_{\frac{1}{2}}^{(0)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(m)}(W_l^2)]_{\alpha l} = 0, \quad m = 0, 1, 2, \dots; \\ [S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(1)}(W_l^2)]_{\alpha l} = \\ = -[S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2)]_{\alpha l} = -16 M_{\alpha} M_l \Omega_{\alpha l}^{(1)}(1); \\ [S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(1)}(W_l^2)]_{\alpha l} = \\ = -[S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2)]_{\alpha l} = 16 M_{\alpha} M_l^2 \left\{ \Omega_{\alpha l}^{(1)}(2) - \frac{5}{2} \Omega_{\alpha l}^{(1)}(1) \right\}; \\ [S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2)]_{\alpha l} = 16 M_{\alpha} M_l \left\{ \left[\frac{5}{2} (M_{\alpha} - M_l) + \frac{35}{4} M_l^2 \right] \Omega_{\alpha l}^{(1)}(1) - \right. \\ \left. - 5 M_l^2 \Omega_{\alpha l}^{(1)}(2) + M_l^2 \Omega_{\alpha l}^{(1)}(3) + M_{\alpha} M_l \Omega_{\alpha \lambda}^{(2)}(2) \right\};$$

$$[S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(2)}(W_l^2)]_{\alpha l} = 16M_{\alpha}^2 M_l^2 \left\{ -\frac{35}{4} \Omega_{\alpha l}^{(1)}(1) + \right. \\ \left. + 5 \Omega_{\alpha l}^{(1)}(2) - \Omega_{\alpha l}^{(1)}(3) + \Omega_{\alpha l}^{(2)}(2) \right\};$$

$$[S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(3)}(W_l^2)]_{\alpha l} = 8M_{\alpha}^3 M_l \left\{ -\frac{35}{4} \Omega_{\alpha l}^{(1)}(1) + 7 \Omega_{\alpha l}^{(1)}(2) - \right. \\ \left. - \Omega_{\alpha l}^{(1)}(3) \right\} = -[S_{\frac{1}{2}}^{(1)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(3)}(W_{\alpha}^2)]_{\alpha l};$$

$$[S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(3)}(W_l^2)]_{\alpha l} = 8M_{\alpha} M_l^2 \left\{ \left[\frac{315}{8} M_l^2 + \frac{35}{2} (M_{\alpha} - M_l) \right] \Omega_{\alpha l}^{(1)}(1) - \right. \\ - \left[\frac{133}{4} M_l^2 + 7(M_{\alpha} - M_l) \right] \Omega_{\alpha l}^{(1)}(2) + \frac{19}{2} M_l^2 \Omega_{\alpha l}^{(1)}(3) - \\ \left. - M_l^2 \Omega_{\alpha l}^{(1)}(4) + 7M_{\alpha} M_l \Omega_{\alpha l}^{(2)}(2) - 2M_{\alpha} M_l \Omega_{\alpha l}^{(2)}(3) \right\};$$

$$[S_{\frac{1}{2}}^{(2)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(3)}(W_l^2)]_{\alpha l} = 8M_{\alpha}^3 M_l^2 \left\{ -\frac{315}{8} \Omega_{\alpha l}^{(1)}(1) + \frac{133}{4} \Omega_{\alpha l}^{(1)}(2) - \right. \\ \left. - \frac{19}{2} \Omega_{\alpha l}^{(1)}(3) + \Omega_{\alpha l}^{(1)}(4) + 7 \Omega_{\alpha l}^{(2)}(2) - 2 \Omega_{\alpha l}^{(2)}(3) \right\};$$

$$[S_{\frac{1}{2}}^{(3)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(3)}(W_l^2)]_{\alpha l} = 8M_{\alpha} M_l \left\{ \frac{35}{4} \left[(M_{\alpha}^2 + 8M_l^2)(M_{\alpha} - M_l) + \frac{199}{8} M_l \right] \Omega_{\alpha l}^{(1)}(1) - \right. \\ - M_l^2 \left[\frac{411}{4} M_l^2 + 19(M_{\alpha} - M_l) \right] \Omega_{\alpha l}^{(1)}(2) + M_l^2 \left[\frac{169}{4} M_l^2 + 9(M_{\alpha} - M_l) \right] \Omega_{\alpha l}^{(1)}(3) - \\ - 7M_l^4 \Omega_{\alpha l}^{(1)}(4) + \frac{1}{2} M_l^4 \Omega_{\alpha l}^{(1)}(5) + 7M_{\alpha} M_l \left(\frac{7}{2} M_l^2 + M_{\alpha}^2 \right) \Omega_{\alpha l}^{(2)}(2) - \\ \left. - 14M_{\alpha} M_l^3 \Omega_{\alpha l}^{(2)}(3) + 2M_{\alpha} M_l^3 \Omega_{\alpha l}^{(2)}(4) + \frac{1}{3} M_{\alpha}^2 M_l^2 \Omega_{\alpha l}^{(3)}(3) \right\};$$

$$[S_{\frac{1}{2}}^{(3)}(W_{\alpha}^2), S_{\frac{1}{2}}^{(3)}(W_l^2)]_{\alpha l} = 8M_{\alpha}^3 M_l^3 \left\{ -\frac{3465}{32} \Omega_{\alpha l}^{(1)}(1) + \right. \\ + \frac{441}{4} \Omega_{\alpha l}^{(1)}(2) - \frac{169}{4} \Omega_{\alpha l}^{(1)}(3) + 7 \Omega_{\alpha l}^{(1)}(4) - \frac{1}{2} \Omega_{\alpha l}^{(1)}(5) + \\ \left. + \frac{63}{2} \Omega_{\alpha l}^{(2)}(2) - 14 \Omega_{\alpha l}^{(2)}(3) + 2 \Omega_{\alpha l}^{(2)}(4) - \frac{4}{3} \Omega_{\alpha l}^{(3)}(3) \right\};$$

$$R_{\alpha 0} = 0;$$

$$R_{\alpha 1} = \frac{n_{\alpha}}{\sum_{\alpha} n_{\alpha}} \sum_i \left(\frac{3}{2} + \tilde{\epsilon}_i \right) K_i^{(0)} - J_1;$$

$$R_{\alpha m} = -J_{\alpha m} \quad (m \geq 2);$$

$$J_{\alpha i} = \frac{1}{2} \sum_r \sum_{\beta \gamma \delta} A_i \left[\left(\frac{m_{\gamma} m_{\delta}}{m_{\alpha} m_{\beta}} \right)^{1/2} e^{\tilde{\epsilon}} n_{\gamma} n_{\delta} - n_{\alpha} n_{\beta} \right], \quad i = 1, 2, \dots,$$

here $\tilde{\epsilon}_i = \epsilon_i/kT$, $\tilde{\epsilon} = \tilde{\epsilon}_{\gamma} + \tilde{\epsilon}_{\delta} - \tilde{\epsilon}_{\alpha} - \tilde{\epsilon}_{\beta}$. Coefficients A_i are the following:

$$A_1 = 4M_{\beta} [3\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(0) - 2\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(1)];$$

$$A_2 = M_{\beta}^2 [15\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(0) - 20\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(1) + 4\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(2)];$$

$$A_3 = M_{\beta}^3 \left[\frac{35}{2} \tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(0) - 35\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(1) + 14\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(2) - \frac{4}{3} \tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(3) \right],$$

where $\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(h)$ are the collision integrals which were introduced in reference [1]. Note that in this approximation, since probability $\tilde{P}_{\alpha\beta}^{\gamma\delta}(g_{\alpha\beta}, 0, \varphi)$

has been normalized to unity, the nonisotropy of the dissociation of the activated complex has no effect on calculated results. The rate of the reaction in the first approximation will be

$$K_{\alpha}^{(0)} = \frac{1}{4} \sum_r \sum_{\beta \gamma \delta} \int \int \int \int \int (f_{\gamma}^{(0)} f_{\delta}^{(0)} - f_{\alpha}^{(0)} f_{\beta}^{(0)}) \tilde{P}_{\alpha\beta}^{\gamma\delta} g_{\alpha\beta} b \sin \theta db d\theta d\epsilon d\varphi \times \\ \times d\vec{v}_{\alpha} d\vec{v}_{\beta} = \frac{1}{2} \sum_r \sum_{\beta \gamma \delta} 4\tilde{\Omega}_{\alpha\beta}^{\gamma\delta}(0) \left[\left(\frac{m_{\gamma} m_{\delta}}{m_{\alpha} m_{\beta}} \right)^{1/2} n_{\gamma} n_{\delta} e^{\tilde{\epsilon}} - n_{\alpha} n_{\beta} \right].$$

Note that in $R_{\alpha 1}$:

$$\frac{n_{\alpha}}{\sum_{\alpha} n_{\alpha}} \sum_i \left(\frac{3}{2} + \tilde{\epsilon}_i \right) K_i^{(0)} = -\frac{n_{\alpha}}{p} \sum_r K_{\alpha r}^{(0)} Q_r,$$

where Q_r is the heat of the r th homogeneous reaction. Thus, the the multicomponent mixture correction to the reaction rate due to the heat of reaction has the form $P(E/kT) Q_c^{-E/kT}$ (where $P(E/kT)$ is the polynomial of E/kT). Thus, the evaluation of the effect of the heat of reaction on the reaction rate presented in [3] is not valid.

In order to study the rate of convergence of (2), consider the simplest reaction, $A+A \rightarrow C+D$, and neglect the reaction products. From conditions (6) and (7), it follows that $t_{\alpha 1} = t_{\alpha 0} = 0$. The bracketed expressions, necessary for three approximations, are the following:

$$\begin{aligned}
 [S_{1/2}^{(1)}(W_\alpha^2), S_{1/2}^{(1)}(W_\alpha^2)]_\alpha &= [S_{1/2}^{(0)}(W_\alpha^2), S_{1/2}^{(m)}(W_\alpha^2)]_\alpha = \\
 &= -[S_{1/2}^{(1)}(W_\alpha^2), S_{1/2}^{(m)}(W_\alpha^2)]_\alpha = 0, \quad m = 0, 1, 2, \dots; \\
 [S_{1/2}^{(2)}(W_\alpha^2), S_{1/2}^{(2)}(W_\alpha^2)]_\alpha &= 2\Omega_\alpha^{(2)}(2); \\
 [S_{1/2}^{(2)}(W_\alpha^2), S_{1/2}^{(3)}(W_\alpha^2)]_\alpha &= \frac{7}{2}\Omega_\alpha^{(2)}(2) - \Omega_\alpha^{(2)}(3); \\
 [S_{1/2}^{(3)}(W_\alpha^2), S_{1/2}^{(3)}(W_\alpha^2)]_\alpha &= \frac{63}{8}\Omega_\alpha^{(2)}(2) - \frac{7}{2}\Omega_\alpha^{(2)}(3) + \frac{1}{2}\Omega_\alpha^{(2)}(4); \\
 [S_{1/2}^{(2)}(W_\alpha^2), S_{1/2}^{(4)}(W_\alpha^2)]_\alpha &= \frac{63}{16}\Omega_\alpha^{(2)}(2) - \frac{9}{4}\Omega_\alpha^{(2)}(3) + \frac{1}{4}\Omega_\alpha^{(2)}(4); \\
 [S_{1/2}^{(3)}(W_\alpha^2), S_{1/2}^{(4)}(W_\alpha^2)]_\alpha &= \frac{693}{64}\Omega_\alpha^{(2)}(2) - \frac{225}{32}\Omega_\alpha^{(2)}(3) + \\
 &+ \frac{25}{16}\Omega_\alpha^{(2)}(4) - \frac{1}{8}\Omega_\alpha^{(2)}(5); \\
 [S_{1/2}^{(4)}(W_\alpha^2), S_{1/2}^{(4)}(W_\alpha^2)]_\alpha &= \frac{9009}{512}\Omega_\alpha^{(2)}(2) - \frac{891}{64}\Omega_\alpha^{(2)}(3) + \frac{269}{64}\Omega_\alpha^{(2)}(4) - \\
 &- \frac{9}{16}\Omega_\alpha^{(2)}(5) + \frac{1}{32}\Omega_\alpha^{(2)}(6) + \frac{1}{24}\Omega_\alpha^{(4)}(4).
 \end{aligned}$$

Henceforth, it is necessary to define explicitly the dependences $p_{\alpha\alpha}^{\alpha\alpha}(g_{\alpha\alpha})$ and $p_{\alpha\alpha}^{00}(g_{\alpha\alpha})$. Let us consider two theories:

$$p_{\alpha\alpha}^{\alpha\alpha} = \begin{cases} 1, & g^2 < g_0^2; \\ 0, & g^2 > g_0^2; \end{cases} \quad p_{\alpha\alpha}^{00} = \begin{cases} 0, & g^2 < g_0^2; \\ 1, & g^2 > g_0^2; \end{cases}$$

$$P_{\alpha\alpha} = \begin{cases} 1, & g_{11}^2 < g_0^2; \\ 0, & g_{11}^2 > g_0^2; \end{cases} \quad P_{\alpha\alpha}^{r00} = \begin{cases} 0, & g_{11}^2 < g_0^2; \\ 1, & g_{11}^2 > g_0^2, \end{cases} \quad (9)$$

where \vec{g}_{11} is the velocity along the line of centers of the molecules during the collision; $g_0^2 = E/kT$. When E is the activation energy, it is possible to show that case (9) corresponds to the choice of the probability:

$$P_{\alpha\alpha}^{r00} = \begin{cases} 0, & g^2 < g_0^2; \\ 1 - g_0^2/g^2, & g^2 > g_0^2. \end{cases}$$

The reaction rate in the i^{th} approximation will be

$$K_{\alpha}^{(i)} = K_{\alpha}^{(0)} \left(1 + \frac{\sum_{m=2}^i t_{\alpha m} J_m}{4n_{\alpha}^2 \Omega_{\alpha}(0)} \right), \quad i = 2, 3, 4, \dots$$

The results of these calculations are summarized in the table.

The table shows that the first approximation is sufficient for practical purposes for calculating the reaction rate in the most interesting range, $E/kT = \tilde{E}$. With large \tilde{E} values, the series K_{α} converges more slowly. The boundary of the convergence region can be evaluated from the conditions $|t_1| = |t_2|$ when using two approximations. For the first and second theories, we obtain $\tilde{E} \approx 16.8$ and $\tilde{E} \approx 14.1$ respectively. The point of minimum $K/K^{(0)}$ for small values of \tilde{E} is $\tilde{E} = 5.7$ by the first theory and $\tilde{E} = 4.4$ by the second theory.

E/kT	First theory $K/K^{(0)}$		Second theory $K/K^{(0)}$	
	1st approx- imation	2nd approx- imation	1st approx- imation	2nd approx- imation
3	0,92943	0,92936	0,9358	0,9348
4	0,8089	0,8038	0,9130	0,9128
5	0,74205	0,73408	0,9144	0,9143
7	0,7709	0,7570	0,9499	0,9470
9	0,8744	0,8541	0,9801	0,9756

Commas represent decimal points.

The third approximation for the first theory (when \tilde{E} equals 5, 7 and 9) gives $K/K^{(0)}$ equal to 0.73543, 0.7514, and 0.8479, respectively.

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